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(54) Energy-induced dual curable compositions.

(57) An energy polymerizable composition comprises at least one ethylenically-unsaturated monomer, one of polyurethane precursors, and at least one epoxy monomer, and a curing agent comprising an organometallic compound, and an onium salt.

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ENERGY-INDUCED DUAL CURABLE COMPOSITIONS

FIELD OF THE INVENTION

This invention relates to an energy-polymerizable composition comprising an ethylenically-unsaturated monomer and either polyurethane precursors or an epoxy monomer, and as curing agent a combination of an organometallic compound and an oxidizing agent, and a method therefor. In a further aspect, cured articles comprising the composition of the invention are disclosed. The compositions are useful, for example, as protective coatings, binders for magnetic media or abrasives, adhesives, and in graphic arts applications.

Background Of The Invention

Various polymeric coatings and articles are produced in processes involving the use of organic solvents. There is an intense effort by law makers, researchers, and industry to promote high and 100% solids formulations to reduce or eliminate the use of such solvents and the attendant costs and environmental contamination. These processes require a latent catalyst or latent reaction promoter which can be activated in a controlled fashion.

Thermal curing of polyurethane precursors using reaction promoters such as tin salts and tertiaryamines is known in the art. Curing of polymerizable mixtures of polyisocyanates with polyols (referred to as polyurethane precursors) using thermally latent catalysts is known in the art (see for example U.S. Patent Nos. 4,521,545, and 4,582,861).

Photocuring of urethane (meth)acrylates is well known (see T. A. Speckhard, K.K.S. Hwang, S.B. Lin, S.Y. Tsay, M. Koshiba, Y.S. Ding, S.L. Cooper J. Appl. Polymer Science, 1985, 30, 647-666; C. Bluestein Polym.-Plast. Technol. Eng. 1981, 17, 83-93), and photocuring of polyurethane precursors using diazonium salts, tertiaryamine precursors, and organotin compounds is also known (see U.S. Patent Nos. 4,544,466, 4,549,945 and EP 28,696, Derwent abstract). All of these methods suffer from one or more of the following disadvantages: sensitivity to oxygen, requirement of ultraviolet and/or high intensity light, the need for modified resins, loss or dilution of urethane properties, low activity, poor solubility, and poor potlife.

The dual curing of acrylate/urethane precursor mixtures is known but these curing methods are not entirely photoactivated nor are any methods known that provide for the simultaneous curing of the urethane precursors and acrylates (see U.S. Pat. 4,342,793 and Roesler, Modern Paint and Coatings, April, 1986, pages 46-55).

The prior art discloses processes for the polymerization of epoxy materials. It is further known that a metallocene, such as ferrocene, can be used as a curing accelerator for epoxy materials (U.S. Patent No. 3,705,129). U.S. Patent Nos. 3,709,861, 3,714,006, 3,867,354 and 4,237,242 relate to the use of transition metal complexes in the reaction between polyepoxides and polyfunctional curing additives, but they do not teach the polymerization of epoxide group-containing compositions not containing a curing additive. The polymerization of epoxide group-containing materials is also known. Among such processes are those in which the polymerization catalyst is a radiation-sensitive onium salt of a Lewis acid (e.g. diazonium salts as is described in U.S. Patent No. 3,794,576 and U.S. Patent No. 4,080,274, halonium salts as is disclosed in U.S. Patent No. 4,026,705, and the onium salts of Group VIA elements, particularly the sulfonium salts, as are disclosed in U.S. Patent No. 4,058,400), or a dicarbonyl chelate compound of a Group IIIA-VA element as is disclosed in U.S. Patent No. 4,086,091. These compositions are limited to ultraviolet radiation for polymerization. Furthermore, the dicarbonyl chelates are moisture sensitive.

U.S. Patent No. 4,216,288 teaches the thermal curing of cationically polymerizable compositions using onium salts and reducing agents.

Radiation dual curable compositions containing ethylenically unsaturated monomers and epoxy monomers have been described in U.S. Patent Nos. 4,156,035, 4,227,978, and 4,623,676. These compositions include onium salts combined with organic compounds as the curing agent, but do not contain any organometallic compounds.

Energy polymerizable compositions comprising ionic salts of organometallic complex cations and cationically sensitive materials and the curing thereof has been taught (see European Patent Application Nos. 109,851, 1984, Derwent abstract; 094,915, 1983, Derwent abstract; and 094,416, 1983, Derwent abstract).

Neutral organometallic compounds have been used in combination with ... for the photocuring of ethylenically-unsaturated monomers (G. Smets, Pu... (1981); H.M. Wagner, M.D. Purbrick, J. Photograph Science, 29, 230-235 ...

The use of certain photosensitizers with onium salts for initiation of ... unsaturated monomers is also well known in the art. This technique has ... duplication, copying, and other imaging systems (see J. Kosar in Light Se... Application of Nonsilver Halide Photographic processes, Wiley, New York ... salts have been previously described for use as photoinitiators in addition p... U.S. Patent Nos. 3,729,313, 3,741,769, 3,808,006, 4,228,232, 4,250,053 an... Baumann, Wiss. Z. Tech. Hochsch. Leuna-Merseburg, 26, 439 (1984); H. B... and U. Lammel, J. Prakt. Chem., 326 (3), 415 (1984); and H. Bauman... Polym. J., 22 (4), 313 (April 3, 1986).

Summary of the Invention

Briefly, the present invention provides an en... polymer... ethylenically-unsaturated monomer and either polyur... precurs... curing agent a combination of a organometallic compo... and an oni... as protective and decorative coatings, inks, adhesives, binders fo... restorative and sealant applications, and in imaging applications.

It is believed not known in the art that latent, energy induced sim... curing of ethylenically-unsaturated monomers, in combination with eit... monomers, can be achieved by using as curing agent a combinatio... an onium salt oxidizing agent.

Advantages of comp...tions of the present invention when utiliz... tions include:

An industrial process innovation is disclosed that will reduce ... industrial solvent waste while reducing energy consumption.

Radiation processing, particularly utilizing electron beam and ... capability for penetrating and polymerizing thick and pigmented ...

More readily available monomers can be used in place of func... thereby resulting in lower viscosity monomer solutions which a... solutions.

Expanding the scope of curable monomers to include ... increased flexibility in designing coatings with specific properties.

In this application:

"dual curing" means the simultaneous energy-induced curing ... combination with one of polyurethane precursors and epoxy mon...

"energy-induced curing" means curing by means of electroma... accelerated particles (including electron beam), and thermal (infra...

"ethylenically unsaturated monomer" means those ... that ...

"catalytically-effective amount" means a quantity s... to effe... tion to a polymerized product at least to a degree to cause an increa...

"organometallic compound" means a chemical substance in which ... group is bonded to a metal atom ("Basic Inorganic Chemistry", F.A. ... 1976, p 497);

"polyurethane precursors" means a mixture of one or more monom... and polyisocyanates, and one or more monomers of the type w... bearing at least two isocyanate-reactive hydrogen atoms may be ... of isocyanate groups to isocyanate-reactive hydrogen atoms is 1:2 ...

"polymerizable mixture" means a mixture where the ratio of ... (polyurethane precursors or epoxy compounds) is 1:99 to 99:1.

"bridging ligand" means a ligand that bonds to two or more meta... metal bonds.

Neutral organometallic compounds have been used in combination with neutral halogenated compounds for the photocuring of ethylenically-unsaturated monomers (G. Smets, Pure G. Appl. Chem., 53, 611-615 (1981); H.M. Wagner, M.D. Purbrick, J. Photograph Science, 29, 230-235.

The use of certain photosensitizers with onium salts for initiation of polymerization of ethylenically unsaturated monomers is also well known in the art. This technique has found applications in printing, duplication, copying, and other imaging systems (see J. Kosar in Light Sensitive Systems: Chemistry and Application of Nonsilver Halide Photographic processes, Wiley, New York, 1965, pp 158-193). Aryliodonium salts have been previously described for use as photoinitiators in addition-polymerizable compositions. (See U.S. Patent Nos. 3,729,313, 3,741,769, 3,808,006, 4,228,232, 4,250,053 and 4,428,807; H. J. Timpe and H. Baumann, Wiss. Z. Tech. Hochsch. Leuna-Merseburg, 26, 439 (1984); H. Baumann, B. Strehmel, H. J. Timpe and U. Lammel, J. Prakt. Chem., 326 (3), 415 (1984); and H. Baumann, U. Oertel and H. J. Timpe, Euro. Polym. J., 22 (4), 313 (April 3, 1986).

Summary of the Invention

Briefly, the present invention provides an energy polymerizable composition comprising an ethylenically-unsaturated monomer and either polyurethane precursors or an epoxy monomer, and as curing agent a combination of a organometallic compound and an onium salt. The compositions are useful as protective and decorative coatings, inks, adhesives, binders for magnetic media or abrasives, in restorative and sealant applications, and in imaging applications.

It is believed not known in the art that latent, energy induced, simultaneous, preferably solventless dual curing of ethylenically-unsaturated monomers, in combination with either polyurethane precursors or epoxy monomers can be achieved by using as curing agent a combination of an organometallic compound and an onium salt oxidizing agent.

Advantages of compositions of the present invention when utilized in 100% reactive coating compositions include:

An industrial process innovation is disclosed that will reduce, minimize, or eliminate the generation of industrial solvent waste while reducing energy consumption.

Radiation processing, particularly utilizing electron beam and photogenerated catalysts, has potential capability for penetrating and polymerizing thick and pigmented coatings.

More readily available monomers can be used in place of functionalized oligomers (used in the prior art) thereby resulting in lower viscosity monomer solutions which are easier to coat than more viscous oligomer solutions.

Expanding the scope of curable monomers to include polyisocyanates/polyols and epoxides allows increased flexibility in designing coatings with specific properties.

In this application:

"dual curing" means the simultaneous energy-induced curing of ethylenically-unsaturated monomers in combination with one of polyurethane precursors and epoxy monomers.

"energy-induced curing" means curing by means of electromagnetic radiation (ultraviolet and visible) accelerated particles (including electron beam), and thermal (infrared and heat) means.

"ethylenically unsaturated monomer" means those monomers that polymerize by a free-radical mechanism.

"catalytically-effective amount" means a quantity sufficient to effect polymerization of the curable composition to a polymerized product at least to a degree to cause an increase in the viscosity of the composition;

"organometallic compound" means a chemical substance in which at least one carbon atom of an organic group is bonded to a metal atom ("Basic Inorganic Chemistry", F.A. Cotton, G. Wilkinson, Wiley, New York, 1976, p 497).

"polyurethane precursors" means a mixture of one or more monomers of the type including diisocyanates and polyisocyanates, and one or more monomers of the type including diols and polyols. Compounds bearing at least two isocyanate-reactive hydrogen atoms may be substituted for diols and polyols; the ratio of isocyanate groups to isocyanate-reactive hydrogen atoms is 1:2 to 2:1.

"polymerizable mixture" means a mixture where the ratio of (ethylenically-unsaturated compounds):(polyurethane precursors or epoxy compounds) is 1:99 to 99:1.

"bridging ligand" means a ligand that bonds to two or more metals in the presence or absence of metal-metal bonds.

"polyisocyanate" means an aliphatic or aromatic isocyanate having 2 or more isocyanate groups;
"polyol" means an aliphatic or aromatic compound containing 2 or more hydroxyl groups; and
"onium salt" means salts of cationic compounds such as diazonium, halonium, and hypervalent Group VIA
elements.

Detailed Disclosure of the Invention

More specifically, in a preferred embodiment this invention describes an energy polymerizable com-
position comprising in the range of 99 to 1 weight percent an ethylenically-unsaturated monomer and 1 to
99 weight percent of either polyurethane precursors or an epoxy monomer and a bicomponent curing agent
therefor, the curing agent comprising

1) an organometallic compound having the structure

$L^1L^2L^3M$

wherein
L^1 represents none, or 1 to 12 ligands contributing pi-electrons that can be the same or different ligand
selected from substituted and unsubstituted acyclic and cyclic unsaturated compounds and groups and
substituted and unsubstituted carbocyclic aromatic and heterocyclic aromatic compounds, each capable of
contributing 2 to 12 pi-electrons to the valence shell of M;
L^2 represents none, or 1 to 24 ligands that can be the same or different contributing an even number of
sigma-electrons selected from mono-, di-, and tri-dentate ligands, each donating 2, 4, or 6 sigma-electrons
to the valence shell of M;
L^3 represents none, or 1 to 12 ligands that can be the same or different, each contributing no more than
one sigma electron each to the valence shell of each M;
M represents 1 to 4 of the same or different metal atoms selected from the elements of Periodic Groups
IVB, VB, VIB, VIIB, and VIIIB (commonly referred to as transition metals);

with the proviso that said organometallic compounds contains at least one of a metal-metal sigma bond and
L^3, and with the proviso that L^1, L^2, L^3, and M are chosen so as to achieve a stable configuration, and

2) an onium salt oxidizing agent having the structure II

AX II

wherein
A is an organic cation selected from those described in U.S. Patent Nos. 3,708,296, 3,729,313, 3,741,769,
3,794,576, 3,808,006, 4,026,705, 4,058,401, 4,069,055, 4,101,513, 4,216,288, 4,394,403, and 4,623,676,
preferably selected from diazonium, iodonium, and sulfonium cations, while more preferably A is selected
from diphenyliodonium, triphenylsulfonium and phenylthiophenyl diphenylsulfonium, and
X is an anion, the counterion of the onium salts including those in which X is an organic sulfonate, or
halogenated metal or metalloid, such as $CH_3SO_3^-$, CF_3SO^-, $C_6H_5SO_3^-$, p-toluenesulfonate, p-chloroben-
zenesulfonate and related isomers and the like, and
those in which X has the formula DZ_r, wherein D is a metal from Groups IB to VIIIB or a metal or metalloid
from Groups IIIA to VA of the Periodic Chart of Elements, Z is a halogen atom, and r is an integer having a
value of 1 to 6. Preferably, the metals are copper, zinc, titanium, vanadium, chromium, manganese, iron,
cobalt, or nickel and the metalloids preferably are boron, aluminum, antimony, tin, arsenic, and phos-
phorous. Preferably, the halogen, Z, is chlorine or fluorine. Illustrative of suitable anions are BF_4^-, PF_6^-,
AsF_6^-, SbF_6^-, $FeCl_4^-$, $SnCl_6^-$, SbF_5^-, [illegible], $GaCl_4^-$, InF_4^-, TiF_6^-, etc. Preferably, the anions are
$CF_3SO_3^-$, BF_4^-, PF_6^-, SbF_6^-, SbF_5OH^-, AsF_6^- and $SbCl_6^-$.

The curing agent can be present in the range of 0.1 to 20, preferably 0.1 to 10 weight percent of the
total composition. The ratio of organometallic compound to onium salt is in the range of 10:1 to 1:10 by
weight, preferably 5:1 to 1:5 by weight.

The present invention also provides a process for the polymerization of ethylenically-unsaturated
monomers in combination with one of polyurethane precursors and epoxy monomers comprising the steps
of

(a) providing a mixture of at least one ethylenically-unsaturated monomers and either polyurethane
precursors or an epoxy compound.

(b) adding to said mixture a combination of a catalytically effective amount
comprising an organometallic compound and an onium salt (and all permutations of the
aforementioned components), thereby forming a polymerizable mixture, and

(c) allowing the mixture to polymerize or adding energy to the mixture to effect pol

In a further aspect, there is also provided a method for preparing coated articles
composition of the invention comprising the steps of:

(a) providing a substrate,

(b) coating an energy polymerizable mixture as described above to the substrate
in the art, such as bar, knife, reverse roll, knurled roll, or spin coatings, or by dipping
and the like, with or without a coating solvent, and

(c) applying energy (after evaporation of solvent, if present) to the article to cause
of the coating.

In a still further aspect, there are also provided shaped articles comprising the poly
the invention. The articles can be provided, for example, by techniques such as moldi
casting, and extrusion. Applying energy to the mixture causes polymerization and
shaped article.

It is not preferred, but it may be desirable to add solvent to solubilize con
processing. Solvent, preferably an organic solvent in an amount up to [illegible] weight per
the range of 0 to 90 weight percent, most preferably in the ra[illegible] to 75
polymerizable composition can be used.

There are restrictions on the total sum of electrons donated by the ligands, L
the valence electrons possessed by the metal. For most organometallic comp
tramolecular metal-metal bonding, this sum is governed by the "eighteen electron r
46, 811 (1969)]. This rule is sometimes called the "nine orbital rule", "the effecti
"rare gas rule". This rule states that the most stable organometallic compo
compounds in which the sum of the electrons donated by the ligands and the m
skilled in the art, however, know that there are exceptions to this rule and that org
having a sum of 16, 17, 19 and 20 electrons are also known. Therefore, organ
including intramolecular metal-metal bonding are described by formula I, in which
a total sum of 16, 17, 18, 19, or 20 electrons in the valence shell are included
invention.

For compounds described in formula I in which intramolecular metal-met
departure from the "eighteen electron rule" can occur. It has been proposed
departure from the "eighteen electron rule" in these tra
5305 (1978)] that the departure from the "eighteen electron rule" in these tra
due to the metal-metal interactions destabilizing the metal p orbitals to an
unavailable for ligand bonding. Hence, rather than count electrons around eac
cluster, cluster valence electrons (CVE) are counted. A dinuclear compound
trinuclear compound, 48 CVEs, and a tetranuclear compound, having tetra
planar geometry is seen to have 60, 62, or 64 CVEs, respectively. Those skille
that there are exceptions to this electron counting method and that orga
compounds having a sum of 42, 44, 46, 50 CVEs for a trinuclear compound and
compound are also known. Therefore, di, tri, or tetranuclear organometallic co
formula I in which the complexed metal cluster, MM, MMM, or MMMM, has a tota
50; or 58, 60, 62, 64 CVEs in the valence shell, respectively, [illegible] included
invention.

Illustrative examples of organometallic compounds according to formula I include

$[CpFe(CO)_2]_2$
$Mn_2(CO)_{10}$
$[CpMo(CO)_3]_2$
$[CpW(CO)_3]_2$
$Re_2(CO)_{10}$
$Co_4(CO)_{12}$
$Co_2(CO)_8$
$CpFe(CO)_2SnPh_3$
$CpFe(CO)_2GePh_3$
$[CpFe(CO)_2]_2SnPh_2$
$CpMo(CO)_3SnPh_3$
$(CO)_5MnSnPh_3$

(b) adding to said mixture a combination of a catalytically effective amount of a curing agent comprising an organometallic compound and an onium salt (and all permutations of the order of mixing the aforementioned components), thereby forming a polymerizable mixture, and

(c) allowing the mixture to polymerize or adding energy to the mixture to effect polymerization.

In a further aspect, there is also provided a method for preparing coated articles containing the cured composition of the invention comprising the steps of:

(a) providing a substrate,

(b) coating an energy polymerizable mixture as described above to the substrate by methods known in the art, such as bar, knife, reverse roll, knurled roll, or spin coatings, or by dipping, spraying, brushing, and the like, with or without a coating solvent, and

(c) applying energy (after evaporation of solvent, if present) to the article to cause the polymerization of the coating.

In a still further aspect, there are also provided shaped articles comprising the polymerizable mixture of the invention. The articles can be provided, for example, by techniques such as molding, injection molding, casting, and extrusion. Applying energy to the mixture causes polymerization and provides the cured shaped article.

It is not preferred, but it may be desirable to add solvent to solubilize components and aid in processing. Solvent, preferably an organic solvent, in an amount up to 99 weight percent, but preferably in the range of 0 to 90 weight percent, most preferably in the range of 0 to 75 weight percent, of the polymerizable composition can be used.

There are restrictions on the total sum of electrons donated by the ligands, L^1, L^2, L^3 of formula I and the valence electrons possessed by the metal. For most organometallic compounds not involving intramolecular metal-metal bonding, this sum is governed by the "eighteen electron rule" [see J. Chem. Ed., 46, 811 (1969)]. This rule is sometimes called the "nine orbital rule", "the effective number rule", or the "rare gas rule". This rule states that the most stable organometallic compounds tend to be those compounds in which the sum of the electrons donated by the ligands and the metal is eighteen. Those skilled in the art, however, know that there are exceptions to this rule and that organometallic compounds having a sum of 16, 17, 19, and 20 electrons are also known. Therefore, organometallic compounds not including intramolecular metal-metal bonding are described by formula I, in which complexed metals having a total sum of 16, 17, 18, 19, or 20 electrons in the valence shell are included within the scope of the invention.

For compounds described in formula I in which intramolecular metal-metal bonding exists serious departure from the "eighteen electron rule" can occur. It has been proposed [J. Amer. Chem. Soc. 100, 5305 (1978)] that the departure from the "eighteen electron rule" in these transition metal compounds is due to the metal-metal interactions destabilizing the metal p orbitals to an extent to cause them to be unavailable for ligand bonding. Hence, rather than count electrons around each metal separately in a metal cluster, cluster valence electrons (CVE) are counted. A dinuclear compound, is seen to have 34 CVEs, a trinuclear compound, 48 CVEs, and a tetranuclear compound, having tetrahedron, butterfly, and square planar geometry is seen to have 60, 62, or 64 CVEs, respectively. Those skilled in the art, however, know that there are exceptions to this electron counting method and that organometallic complex cluster compounds having a sum of 42, 44, 46, 50 CVEs for a trinuclear compound and 58 CVEs for a tetranuclear compound are also known. Therefore, di, tri, or tetranuclear organometallic compounds are described by formula I in which the complexed metal cluster, MM, MMM, or MMMM has a total sum of 34, 42, 44, 46, 48, 50, or 58, 60, 62, 64 CVEs in the valence shell, respectively, and are included within the scope of this invention.

Illustrative examples of organometallic compounds according to formula I include:

$[CpFe(CO)_2]_2$
$Mn_2(CO)_{10}$
$[CpMo(CO)_3]_2$
$[CpW(CO)_3]_2$
$Re_2(CO)_{10}$
$Co_4(CO)_{12}$
$Co_2(CO)_8$
$CpFe(CO)_2SnPh_3$
$CpFe(CO)_2GePh_3$
$[CpFe(CO)_2]_2SnPh_2$
$CpMo(CO)_3SnPh_3$
$(CO)_5MnSnPh_3$

$[(CO)_5Mn]_3SnPh_3$
$CpFe(CO)_2PbPh_3$
$(CO)_5MnPbPh_3$
$(CO)_5ReSnPh_3$
$CpPtMe_3$
$CpW(CO)_3Me$
$Cp(CO)_3W\text{-}Mo(CO)_3Cp$
$Cp(CO)_3Mo\text{-}Mn(CO)_5$
$Cp(CO)_3Mo\text{-}Re(CO)_5$
$Cp(CO)_3W\text{-}Mn(CO)_5$
$Cp(CO)_3W\text{-}Re(CO)_5$
$Cp(CO)_3Mo\text{-}Co(CO)_4$
$Cp(CO)_3W\text{-}Co(CO)_4$
$Cp(CO)_3Mo\text{-}Fe(CO)_2Cp$
$(CO)_5Mn\text{-}Fe(CO)_2Cp$
$Cp(CO)_3W\text{-}Fe(CO)_2Cp$
$[CpMo(CO)_2PPh_3]_2$
$Mn_2(CO)_9PPh_3$
$Mn_2(CO)_8(PPh_3)_2$
$(CO)_5Mn\text{-}Re(CO)_5$
$Mn_2(CO)_8$ (1,10-phenanthroline)
$[CpFe(CO)_2]_4Si$
$Re_2(CO)_8$(1,10-phenanthroline)
$Re_2(CO)_8$(2,2'-biquinoline)
$Fe_3(CO)_{12}$
$Ru_3(CO)_{12}$
$Os_3(CO)_{12}$
$Ru_3(CO)_{11}PPh_3$
$Ru_3(CO)_{10}(Ph_2P\text{-}CH_2CH_2\text{-}PPh_2)$
$Fe_2Ru(CO)_{12}$
$Ir_4(CO)_{12}$
$[CpNi(CO)]_2$
$CpFe(CO)_2CH_2Ph$
$CpFe(CO)_2(COPh)$
$CpFe(CO)_2(SiPh_3)$
$[CP^*Fe(CO)_2]_2$
$Cp(CO)_2Fe\text{-}Fe(CO)(PPh_3)Cp$
$(MeCp)PtMe_3$
$(Me_3SiCp)PtMe_3$
$Cp(CO)_3Mo\text{-}Mo(CO)_2(PPh_3)Cp$

wherein:
Me is methyl
Ph is phenyl
Cp is eta^5-cyclopentadienyl
Cp* is eta^5-pentamethylcyclopentadienyl

A wide variety of monomers can be energy polymerized using the curing agent of the invention. Suitable compounds containing at least one ethylenically-unsaturated double bond, can be monomers and/or oligomers such as (meth)acrylates, (meth)acrylamides, and vinyl compounds, and are capable of undergoing addition polymerization. Such monomers include mono-, di-, or poly- acrylates and methacrylates such as methyl acrylate, methyl methacrylate, ethyl acryate, isopropyl methacrylate, n-hexyl acrylate, stearyl acrylate, allyl acrylate, glycerol diacrylate, glycerol triacrylate, ethyleneglycol diacrylate, diethyleneglycol diacrylate, triethyleneglycol dimethacrylate, 1,3-propanediol diacrylate, 1,3-propanediol dimethacrylate, trimethylolpropane triacrylate, 1,2,4-butanetriol trimethylacrylate, 1,4-cyclohexanediol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, sorbitol hexacrylate, bis[1-(2-acryloxy)]-p-ethoxyphenyldimethylmethane, bis[1-(3-acryloxy-2-hydroxy)]-p-propoxyphenyl-dimethylmethane, tris-hydroxyethylisocyanurate trimethacrylate, the bis-acrylates and bis-methacrylates of polyethylene glycols of molecular weight 200-500, copolymerizable mixtures of acrylated monomers such as those of U.S. Patent No. 4,652,274, and acrylated oligomers such as those of U.S.

Patent No. 4,642,126, unsaturated amides such as acrylamide, methylene bis-acrylamide, methylene bis-methacrylamide, 1,6-hexamethylene bis-acrylamide, diethylene triamine tris-acrylamide and beta-methacrylaminoethyl methacrylate, and vinyl compounds such as styrene, divinylbenzene, divinyl succinate, divinyl adipate, divinyl phthalate, and vinyl azlactones as disclosed in U.S. Patent No. 4,304,705. Mixtures of two or more monomers can be used if desired.

The polyisocyanate component of the polyurethane precursors that can be cured in the dual curing systems of the present invention may be any aliphatic, cycloaliphatic, araliphatic, aromatic, or heterocyclic polyisocyanate, or any combination of such polyisocyanates. Particularly suitable polyisocyanates correspond to the formula

$Q(NCO)_p$ III

in which p is an integer 2 to 4, and Q represents an aliphatic hydrocarbon di-, tri-, or tetra-radical containing from 2 to 100 carbon atoms, and zero to 50 heteroatoms, a cycloaliphatic hydrocarbon radical containing from 4 to 100 carbon atoms and zero to 50 heteroatoms, an aromatic hydrocarbon radical or heterocyclic aromatic radical containing from 5 to 15 carbon atoms and zero to 10 heteroatoms, or an araliphatic hydrocarbon radical containing from 8 to 100 carbon atoms and zero to 50 heteroatoms. The heteroatoms that can be present in Q include non-peroxidic oxygen, sulfur, non-amino nitrogen, halogen, silicon, and non-phosphino phosphorus.

Examples of polyisocyanates are as follows: ethylene diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethylhexamethylene diisocyanate, 1,12-dodecane diisocyanate, cyclobutane-1,3-diisocyanate, cyclohexane-1,3- and -1,4-diisocyanate and mixtures of these isomers, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl cyclohexane (see German Auslegeschrift No. 1,202,785, U.S. Patent No. 3,401,190), 2,4- and 2,6-hexahydrotolylene diisocyanate and mixtures of these isomers, hexahydro-1,3-and/or -1,4- phenylene diisocyanate, perhydro-2,4'- and/or -4,4'- diphenylmethane diisocyanate, 1,3- and 1,4-phenylene diisocyanate, 2,4- and 2,6-tolylene diisocyanate and mixtures of these isomers, diphenylmethane-2,4'- and/or -4,4'-diisocyanate, naphthylene-1,5-diisocyanate, and the reaction products of four equivalents of the aforementioned isocyanate-containing compounds with compounds containing two isocyanate-reactive groups.

According to the present invention, it is also possible for example to use triphenyl methane-4,4',4''-triisocyanate, polyphenyl polymethylene polyisocyanates described in British Patent Nos. 874,430 and 848,671, m- and p-isocyanatophenyl sulphonyl isocyanates according to U.S. Patent No. 3,454,606, perchlorinated aryl polyisocyanates of the type described, for example, in German Auslegeschrift No. 1,157,601 (U.S. Pat. No. 3,277,138), polyisocyanates containing carbodiimide groups of the type described in U.S. Patent No. 3,152,162 and in German Offenlegungsschrift Nos. 2,504,400, 2,537,685 and 2,552,350, norbornane diisocyanates according to U.S. Patent No. 3,492,330, polyisocyanates containing allophanate groups of the type described, for example, in British Patent No. 994,890, in Belgian Patent No. 761,626 and in Dutch Patent Application No. 7,102,524, polyisocyanates containing isocyanurate groups of the type described, for example in U.S. Patent No. 3,001,973, in German Patent Nos. 1,022,789, 1,222,067 and 1,027,394 and German Offenlegungsschrift Nos. 1,929,034 and 2,004,048, polyisocyanates containing urethane groups of the type described, for example, in Belgian Patent No. 752,261 or in U.S. Patent Nos. 3,394,164 and 3,644,457, polyisocyanates containing acrylated urea groups according to German Patent No. 1,230,778, polyisocyanates containing biuret groups of the type described, for example, in U.S. Patent Nos. 3,124,605, 3,201,372 and 3,124,605 and in British Patent No. 889,050, polyisocyanates produced by telomerization reactions of the type described for example in U.S. Patent No. 3,654,106, polyisocyanates containing ester groups of the type described, for example, in British Patent Nos. 965,474 and 1,072,956, in U.S. Patent No. 3,567,763 and in German Patent No. 1,231,688, reaction products of the above-mentioned diisocyanates with acetals according to German Patent 1,072,385 and polyisocyanates containing polymeric fatty acid esters according to U.S. Patent No. 3,455,883.

It is also possible to use distillation residues having isocyanate groups obtained in the commercial production of isocyanates, optically in solution in one or more of the above-mentioned polyisocyanates. It is also possible to use any mixtures of the above-mentioned polyisocyanates.

Preferred polyisocyanates are hexamethylene diisocyanate, its isocyanurate and its biuret; 4,4'-methylene bis(cyclohexylisocyanate), 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (isophorone diisocyanate), the tolylene diisocyanates and their isocyanurates, the mixed isocyanurate of tolylene diisocyanate and hexamethylene diisocyanate, the reaction product of 1 mol of trimethylol propane and 3 mols of tolylene diisocyanate and also crude diphenyl methane diisocyanate.

Suitable compounds containing at least 2 isocyanate-reactive hydrogen atoms

Patent No 4 642 126; unsaturated amides such as acrylamide, methylene bis-acrylamide, methylene bis-methacrylamide, 1,6-hexamethylene bis-acrylamide, diethylene triamine tris-acrylamide and beta-methacrylaminoethyl methacrylate, and vinyl compounds such as styrene, divinylbenzene diallyl phthalate, divinyl succinate, divinyl adipate, divinyl phthalate, and vinyl azlactones as disclosed in U S Patent No 4 304 705 Mixtures of two or more monomers can be used if desired.

The polyisocyanate component of the polyurethane precursors that can be cured or polymerized in the dual curing systems of the present invention may be any aliphatic, cycloaliphatic, araliphatic, aromatic, or heterocyclic polyisocyanate, or any combination of such polyisocyanates. Particularly suitable polyisocyanates correspond to the formula

$Q(NCO)_p$ III

in which is an integer 2 to 4, and Q represents an aliphatic hydrocarbon di-, tri-, or tetra-radical containing from 2 to carbon atoms, and zero to 50 heteroatoms; a cycloaliphatic hydrocarbon radical containing from 4 to 100 carbon atoms and zero to 50 heteroatoms, an aromatic hydrocarbon radical or heterocyclic aromatic radical containing from 5 to 15 carbon atoms and zero to 10 heteroatoms, or an araliphatic hydrocarbon radical containing from 8 to 100 carbon atoms and zero to 50 heteroatoms. The heteroatoms that can be present in Q include non-peroxidic oxygen, sulfur, non-amino nitrogen, halogen, silicon, and non-phosphino phosphorus.

Examples of polyisocyanates are as follows: ethylene diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, trimethyl hexamethylene diisocyanate, 1,12-dodecane diisocyanate, cyclobutane-1,3-diisocyanate, cyclohexane-1,3- and -1,4-diisocyanate and mixtures of these isomers, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl cyclohexane (see German Auslegeschrift No. 1,202,785, U.S. Patent No. 3,401,190), 2,4- and 2,6-hexahydrotolylene diisocyanate and mixtures of these isomers, hexahydro-1,3-and/or -1,4- phenylene diisocyanate, perhydro-2,4'- and/or -4,4'- diphenylmethane diisocyanate, 1,3- and 1,4-phenylene diisocyanate, 2,4- and 2,6-tolylene diisocyanate and mixtures of these isomers, diphenylmethane-2,4'- and/or -4,4'-diisocyanate, naphthylene-1,5-diisocyanate, and the reaction products of four equivalents of the aforementioned isocyanate-containing compounds with compounds containing two isocyanate-reactive groups.

According to the present invention, it is also possible, for example, to use triphenyl methane-4,4',4''-triisocyanate, polyphenyl polymethylene polyisocyanates described in British Patent Nos. 874,430 and 848,671, m- and p-isocyanatophenyl sulphonyl isocyanates according to U.S. Patent No 3,454,606, perchlorinated aryl polyisocyanates of the type described, for example, in German Auslegeschrift No. 1,157,601 (U S Pat No 3,277,138), polyisocyanates containing carbodiimide groups of the type described in U S Patent No 3,152,162 and in German Offenlegungsschrift Nos 2,504,400, 2,537,685 and 2,552,350, norbornane diisocyanates according to U.S. Patent No 3,492,330, polyisocyanates containing allophanate groups of the type described, for example, in British Patent No 994,890, in Belgian Pat. No 761,626 and in Dutch Patent Application No. 7,102,524, polyisocyanates containing isocyanurate groups of the type described, for example in U.S. Patent No. 3,001,973, in German Patent Nos. 1,022,789, 1,222,067 and 1,027,394 and German Offenlegungsschrift Nos. 1,929,034 and 2,004,048, polyisocyanates containing urethane groups of the type described, for example, in Belgian Patent No. 752,261 or in U.S. Patent Nos. 3,394,164 and 3,644,457, polyisocyanates containing acrylated urea groups according to German Patent No 1,230,778, polyisocyanates containing biuret groups of the type described, for example, in U S. Patent Nos 3,124,605, 3,201,372 and 3,124,605 and in British Patent No. 889,050, polyisocyanates produced by telomerization reactions of the type described for example in U S. Patent No. 3,654,106, polyisocyanates containing ester groups of the type described, for example, in British Patent Nos. 965,474 and 1,072,956, in U S Patent No. 3,567,763 and in German Patent No. 1,231,688, reaction products of the above-mentioned diisocyanates with acetals according to German Patent 1,072,385 and polyisocyanates containing polymeric fatty acid esters according to U S Patent No. 3,455,883.

It is also possible to use distillation residues having isocyanate groups obtained in the commercial production of isocyanates, optionally in solution in one or more of the above-mentioned polyisocyanates. It is also possible to use any mixtures of the above-mentioned polyisocyanates.

Preferred polyisocyanates are hexamethylene diisocyanate, its isocyanurate and its biuret, 4,4'-methylene bis(cyclohexylisocyanate), 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl cyclohexane (isophorone diisocyanate), the tolylene diisocyanates and their isocyanurates, the mixed isocyanurate of tolylene diisocyanate and hexamethylene diisocyanate, the reaction product of 1 mol of trimethylol propane and 3 mols of tolylene diisocyanate and also crude diphenyl methane diisocyanate.

Suitable compounds containing at least 2 isocyanate-reactive hydrogen atoms can be high or low

molecular weight compounds, having a weight average molecular weight, generally from about 50 to 50,000 in addition to compounds containing amino groups, thiol groups or carboxyl groups, are, preferably, compounds containing hydroxyl groups, particularly compounds containing from about 2 to 50 hydroxyl groups and above all, compounds having a weight average molecular weight of from about 500 to 25000, preferably from about 700 to 2000, for example, polyesters, polyethers, polythioethers, polyacetals, polycarbonates poly(meth)acrylates, and polyester amides, containing at least 2, generally from about 2 to 8, but preferably from about 2 to 4 hydroxyl groups, or even hydroxyl-containing prepolymers of these compounds and a less than equivalent quantity of polyisocyanate, of the type known for the production of polyurethanes.

Representatives of the above-mentioned compounds used in accordance with the present invention are described, for example, in High Polymers, Vol XVI, "Polyurethanes, Chemistry and Technology", By Saunders and Frisch, Interscience Publishers, New York London, and Vol I, 1962, pages 32 to 42 and pages 44 to 54 and Vol. II, 1964, pages 5-6 and 198-199, and in Kunststoff-Handbuch, Vol VII, Vieweg-Hochtlen, Carl- HanserVerlag, Munich, 1966, for example, on pages 45 to 71. It is, of course, possible to use mixtures of the above-mentioned compounds containing at least two isocyanate-reactive hydrogen atoms and having a molecular weight of from about 50 to 50,000 for example, mixtures of polyethers and polyesters.

In some cases, it is particularly advantageous to combine low-melting and high-melting polyhydroxyl containing compounds with one another (German Offenlegungsschrift No 2,706,297).

Low molecular weight compounds containing at least two isocyanate-reactive hydrogen atoms (molecular weight from about 50 to 400) suitable for use in accordance with the present invention are compounds preferably containing hydroxyl groups and generally containing from about 2 to 8, preferably from about 2 to 4 isocyanate- reactive hydrogen atoms. It is also possible to use mixtures of different compounds containing at least two isocyanate-reactive hydrogen atoms and having a molecular weight in the range of from about 50 to 400. Examples of such compounds are ethylene glycol, 1,2- and 1,3-propylene glycol, 1,4- and 2,3-butylene glycol 1,5-pentane diol, 1,6-hexane diol, 1,8-octane diol, neopentyl glycol, 1,4-bis-hydroxymethyl cyclohexane 2-methyl-1,3-propane diol, dibromobutene diol (U.S. Patent No 3,723,392), glycerol, trimethylolpropane, 1,2,6-hexanetriol, trimethylolethane, pentaerythritol, quinitol mannitol, sorbitol, diethylene glycol, triethylene glycol, tetraethylene glycol, higher polyethylene glycols, dipropylene glycol, higher polypropylene glycols, dibutylene glycol, higher polybutylene glycols, 4,4'-dihydroxy diphenyl propane and dihydroxy methyl hydroquinone.

Other polyols suitable for the purposes of the present invention are the mixtures of hydroxy aldehydes and hydroxy ketones ("formose") or the polyhydric alcohols obtained therefrom by reduction ("formitol") which are formed in the autocondensation of formaldehyde hydrate in the presence of metal compounds as catalysts and compounds capable of enediol formation as co-catalysts (German Offenlegungsschrift Nos 2,639,084, 2,714,084, 2,714,104, 2,721,186, 2,738,154 and 2,738,512). Solutions of polyisocyanate polyaddition products, particularly solutions of polyurethane ureas containing ionic groups and/or solutions of polyhydrazodicarbonamides, in low molecular weight polyhydric alcohols may also be used as the polyol component in accordance with the present invention (German Offenlegungsschrift No 2,638,759).

Many other compounds containing isocyanate-reactive hydrogen atoms and polyisocyanates are useful in the present invention, and are obvious to those skilled in the art of polyurethane science and technology.

Epoxy compounds that can be cured or polymerized in the dual systems by the curing agents of this invention, using the latter in a catalytically effective amount, are those known to undergo cationic polymerization and include 1,2-, 1,3-, and 1,4-cyclic ethers (also designated as 1,2- 1,3-, and 1,4-epoxides). The 1,2-cyclic ethers are preferred.

The cyclic ethers which can be polymerized in accordance with this invention include those described in "Ring-Opening Polymerizations", Vol. 2, by Frisch and Reegan, Marcel Dekker, Inc (1969). Suitable 1,2-cyclic ethers are the monomeric and polymeric types of epoxides. They can be aliphatic, cycloaliphatic, aromatic, or heterocyclic and will typically have an epoxy equivalency of from 1 to 6, preferably 1 to 3. Particularly useful are the aliphatic, cycloaliphatic, and glycidyl ether type 1,2-epoxides such as propylene oxide, epichlorohydrin, styrene oxide, vinylcyclohexene oxide, vinylcyclohexene dioxide, glycidol, butadiene oxide, glycidyl methacrylate, diglycidyl ether of bisphenol A, cyclohexeneoxide, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate, 3,4-epoxy-6-methylcyclohexylmethyl-3,4-epoxy-6-methylcyclohexanecarboxylate, bis(3,4-epoxy-6-methylcyclohexylmethyl)adipate, dicyclopentadiene dioxide, epoxidized polybutadiene, 1,4-butanediol diglycidyl ether, polyglycidyl ether of phenolformaldehyde resole or novolak resin, resorcinol diglycidyl ether, and epoxy silicones, e.g., dimethylsiloxanes having cycloaliphatic epoxide or glycidyl ether groups.

A wide variety of commercial epoxy resins are available and listed in "Handbook of Epoxy Resins" by

Lee and Neville, McGraw Hill Book Company, New York (1967) and in "Epoxy Resin Technology" by P. F. Bruins, John Wiley & Sons, New York (1968). Representative of the 1,3- and 1,4-cyclic ethers which can be polymerized in accordance with this invention are oxetane, 3,3-bis(chloromethyl)oxetane, and tetrahydrofuran.

In particular, cyclic ethers which are readily available include propylene oxide, oxetane, epichlorohydrin, tetrahydrofuran, styrene oxide, cyclohexeneoxide, vinylcyclohexene oxide, glycidol, glycidyl methacrylate, octylene oxide, phenyl glycidyl ether, 1,2-butane oxide, diglycidyl ether of bisphenol A (e.g., "Epon 828" and "DER 331"), vinylcyclohexene dioxide (e.g., "ERL-4206"), 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate (e.g., "ERL-4221"), 3,4-epoxy-6-methylcyclohexylmethyl 3,4-epoxy-6-methylcyclohexanecarboxylate (e.g., "ERL-4201"), bis(3,4-epoxy-6-methylcyclohexylmethyl)adipate (e.g., "ERL-4289"), aliphatic epoxy modified with polypropylene glycol (e.g., "ERL-4050" and "ERL-4052"), dipentene dioxide (e.g., "ERL-4269"), epoxidized polybutadiene (e.g., "Oxiron 2001"), silicon epoxy (e.g., "Syl-Kem 90"), 1,4-butanediol diglycidyl ether (e.g., Araldite RD-2), polyglycidyl ether of phenolformaldehyde novolak (e.g., "DER-431", "Epi-Rez 521" and "DER-438"), resorcinol diglycidyl ether (e.g., "Kopoxite"), polyglycol diepoxide (e.g., "DER 736"), polyacrylate epoxide (e.g., "Epocryl U-14"), urethane modified epoxide (e.g., "QX3599"), polyfunctional flexible epoxides (e.g., "Flexibilizer 151"), and mixtures thereof as well as mixtures thereof with co-curatives, curing agents, or hardeners which also are well known (see Lee and Neville and Bruins, supra). Representative of the co-curatives of hardeners which can be used are acid anhydrides such as nadic methyl anhydride, cyclopentanetetracarboxylic dianhydride, pyromellitic anhydride, cis-1,2-cyclohexanedicarboxylic anhydride, and mixtures thereof.

As noted above, the organometallic compounds useful in combination with onium salts to provide curing agents useful in the invention have the formula

$L^1L^2L^3M$, I

Ligands L^1 to L^3 are well known in the art of transition metal organometallic compounds.

Ligand L^1 of general formula I is provided by any monomeric or polymeric compound having an accessible unsaturated group, i.e., an ethylenic, $-\overset{|}{C}=\overset{|}{C}-$ group, acetylenic, $-C\equiv C-$ group, or aromatic group which has accessible pi-electrons regardless of the total molecular weight of the compound. By "accessible", it is meant that the compound (or precursor compound from which the accessible compound is prepared) bearing the unsaturated group is soluble in a reaction medium, such as an alcohol, e.g., methanol, a ketone, e.g., methyl ethyl ketone, an ester, e.g., amyl acetate, a halocarbon, e.g., trichloroethylene, an alkane, e.g., decalin, an aromatic hydrocarbon, e.g., anisole, an ether, e.g., tetrahydrofuran, etc., or that the compound is divisible into very fine particles of high surface area so that the unsaturated group (including aromatic group) is sufficiently close to a metal atom to form a pi-bond between that unsaturated group and the metal atom. By polymeric compound, is meant, as explained below, that the ligand can be a group on a polymeric chain.

Illustrative of ligand L^1 are the linear and cyclic ethylenic and acetylenic compounds having less than 100 carbon atoms, preferably having less than 60 carbon atoms, and from zero to 10 hetero atoms selected from nitrogen, sulfur, non-peroxidic oxygen, phosphorous, arsenic, selenium, boron, antimony, tellurium, silicon, germanium, and tin, such as, for example, ethylene, acetylene, propylene, methylacetylene, 1-butene, 2-butene, diacetylene, butadiene, 1,2-dimethylacetylene, cyclobutene, pentene, cyclopentene, hexene, cyclohexene, 1,3-cyclohexadiene, cyclopentadiene, 1,4-cyclohexadiene, cycloheptene, 1-octene, 3,4-dimethyl-3-hexene, and 1-decene, eta^3-allyl, eta^3-pentenyl, norbornadiene, eta^5-cyclohexadienyl, eta^6-cycloheptatriene, eta^8-cyclooctatetraene, and substituted and unsubstituted carbocyclic and heterocyclic aromatic ligands having up to 25 rings and up to 100 carbon atoms and up to 10 hetero atoms selected from nitrogen, sulfur, non-peroxidic oxygen, phosphorous, arsenic, selenium, boron, antimony, tellurium, silicon, germanium, and tin, such as, for example, eta^5-cyclopentadienyl, benzene, mesitylene, hexamethylbenzene, fluorene, naphthalene, anthracene, chrysene, pyrene, eta^7-cycloheptatrienyl, triphenylmethane, paracyclophane, 1,4-diphenylbutane, eta^5-pyrrole, eta^5-thiophene, eta^5-furan, pyridine, gamma-picoline, quinaldine, benzopyran, thiochrome, benzoxazine, indole, acridine, carbazole, triphenylene, silabenzene, arsabenzene, stibabenzene, 2,4,6-triphenylphosphabenzene, eta^5-selenophene, dibenzostannepine, eta^5-tellurophene, phenothiarsine, selenanthrene, phenoxaphosphine, phenarsazine, phenatellurazine, eta^5-methylcyclopentadienyl, eta^5-pentamethylcyclopentadienyl, and 1-phenylborabenzene. Other suitable aromatic compounds can be found by consulting any of many chemical handbooks.

As mentioned before, the ligand can be a unit of a polymer, for example, the phenyl group in polystyrene, poly(styrene-co-butadiene), poly(styrene-co-methyl methacrylate), poly(alpha-methylstyrene), polyvinylcarbazole, and polymethylphenylsiloxane, the cyclopentadiene group in poly(vinylcyclopentadiene)

Lee and Neville, McGraw Hill Book Company, New York (1967) and in "Epoxy Resin Technology" by P. F. Bruins, John Wiley & Sons, New York (1968). Representative of the 1,3- and 1,4-cyclic ethers which can be polymerized in accordance with this invention are oxetane, 3,3-bis(chloromethyl)oxetane, and tetrahydrofuran.

In particular, cyclic ethers which are readily available include propylene oxide, oxetane, epichlorohydrin, tetrahydrofuran, styrene oxide, cyclohexeneoxide, vinylcyclohexene oxide, glycidol, glycidyl methacrylate, octylene oxide, phenyl glycidyl ether, 1,2-butane oxide, diglycidyl ether of bisphenol A (e.g., "Epon 828" and "DER 331"), vinylcyclohexene dioxide (e.g., "ERL-4206"), 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate (e.g., "ERL-4221"), 3,4-epoxy-6-methylcyclohexylmethyl 3,4-epoxy-6-methylcyclohexanecarboxylate (e.g., "ERL-4201"), bis(3,4-epoxy-6-methylcyclohexylmethyl)adipate (e.g., "ERL-4289"), aliphatic epoxy modified with polypropylene glycol (e.g., "ERL-4050" and "ERL-4052"), dipentene dioxide (e.g., "ERL-4269"), epoxidized polybutadiene (e.g., "Oxiron 2001"), silicon epoxy (e.g., "Syl-Kem 90"), 1,4-butanediol diglycidyl ether (e.g., Araldite RD-2), polyglycidyl ether of phenolformaldehyde novolak (e.g., "DER-431", "Epi-Rez 521" and "DER-438"), resorcinol diglycidyl ether (e.g., "Kopoxite"), polyglycol diepoxide (e.g., "DER 736"), polyacrylate epoxide (e.g., "Epocryl U-14"), urethane modified epoxide (e.g., "QX3599"), polyfunctional flexible epoxides (e.g., "Flexibilizer 151"), and mixtures thereof as well as mixtures thereof with co-curatives, curing agents, or hardeners which also are well known (see Lee and Neville and Bruins, supra). Representative of the co-curatives of hardeners which can be used are acid anhydrides such as nadic methyl anhydride, cyclopentanetetracarboxylic dianhydride, pyromellitic anhydride, cis-1,2-cyclohexanedicarboxylic anhydride, and mixtures thereof.

As noted above, the organometallic compounds useful in combination with onium salts to provide the curing agents useful in the invention have the formula

L'L²L³M   I

Ligands L' to L³ are well known in the art of transition metal organometallic compounds.

Ligand L' of general formula I is provided by any monomeric or polymeric compound having an accessible unsaturated group, i.e., an ethylenic, -C=C- group, acetylenic, -C≡C- group, or aromatic group which has accessible pi-electrons regardless of the total molecular weight of the compound. By "accessible" it is meant that the compound (or precursor compound from which the accessible compound is prepared) bearing the unsaturated group is soluble in a reaction medium, such as an alcohol, e.g., methanol; a ketone, e.g., methyl ethyl ketone; an ester, e.g., amyl acetate; a halocarbon, e.g., trichloroethylene; an alkane, e.g., decalin; an aromatic hydrocarbon, e.g., anisole; an ether, e.g., tetrahydrofuran, etc., or that the compound is divisible into very fine particles of high surface area so that the unsaturated group (including aromatic group) is sufficiently close to a metal atom to form a pi-bond between that unsaturated group and the metal atom. By polymeric compound, is meant, as explained below, that the ligand can be a group on a polymeric chain.

Illustrative of ligand L' are the linear and cyclic ethylenic and acetylenic compounds having less than 100 carbon atoms, preferably having less than 60 carbon atoms, and from zero to 10 hetero atoms selected from nitrogen, sulfur, non-peroxidic oxygen, phosphorous, arsenic, selenium, boron, antimony, tellurium, silicon, germanium, and tin, such as, for example, ethylene, acetylene, propylene, methylacetylene, 1-butene, 2-butene, diacetylene, butadiene, 1,2-dimethylacetylene, cyclobutene, pentene, cyclopentene, hexene, cyclohexene, 1,3-cyclohexadiene, cyclopentadiene, 1,4-cyclohexadiene, cycloheptene, 1-octene, 4-octene, 3,4-dimethyl-3-hexene, and 1-decene, eta³-allyl, eta³-pentenyl, norbornadiene, eta⁵-cyclohexadienyl, eta⁶-cycloheptatriene, eta⁸-cyclooctatetraene, and substituted and unsubstituted carbocyclic and heterocyclic aromatic ligands having up to 25 rings and up to 100 carbon atoms and up to 10 hetero atoms selected from nitrogen, sulfur, non-peroxidic oxygen, phosphorous, arsenic, selenium, boron, antimony, tellurium, silicon, germanium, and tin, such as, for example, eta⁵-cyclopentadienyl, benzene, mesitylene, hexamethylbenzene, fluorene, naphthalene, anthracene, chrysene, pyrene, eta⁷-cycloheptatrienyl, triphenylmethane, paracyclophane, 1,4-diphenylbutane, eta⁵-pyrrole, eta⁵-thiophene, eta⁵-furan, pyridine, gamma-picoline, quinaldine, benzopyran, thiochrome, benzoxazine, indole, acridine, carbazole, triphenylene, silabenzene, arsabenzene, stibabenzene, 2,4,6-triphenylphosphabenzene, eta⁵-selenophene, dibenzostannepine, eta⁵-tellurophene, phenothiarsine, selenanthrene, phenoxaphosphine, phenarsazine, phenatellurazine, eta⁵-methylcyclopentadienyl, eta⁵-pentamethylcyclopentadienyl, and 1-phenylborabenzene. Other suitable aromatic compounds can be found by consulting any of many chemical handbooks.

As mentioned before the ligand can be a unit of a polymer, for example the phenyl group in polystyrene, poly(styrene-co-butadiene), poly(styrene-co-methyl methacrylate), poly(alpha-methylstyrene), polyvinylcarbazole, and polymethylphenylsiloxane; the cyclopentadiene group in poly(vinylcyclopentadiene);

the pyridine group in poly(vinylpyridine), etc. Polymers having a weight average molecular weight up to 1,000,000 or more can be used. It is preferable that 5 to 50 percent of the unsaturated or aromatic groups present in the polymer be complexed with metallic cations.

Each ligand L' can be substituted by groups that do not interfere with the complexing of the ligand with the metal atom or which do not reduce the solubility of the ligand to the extent that complexing with the metal atom does not take place. Examples of substituting groups, all of which preferably have less than 30 carbon atoms and up to 10 hetero atoms selected from nitrogen, sulfur, non-peroxidic oxygen, phosphorus, arsenic, selenium, antimony, tellurium, silicon, germanium, tin, and boron include hydrocarbyl groups such as methyl, ethyl, butyl, dodecyl, tetracosanyl, phenyl, benzyl, allyl, benzylidene, ethenyl, and ethynyl; hydrocarbyloxy groups such as methoxy, butoxy, and phenoxy; hydrocarbylmercapto groups such as methylmercapto (thiomethoxy), phenylmercapto (thiophenoxy); hydrocarbyloxycarbonyl such as methoxycarbonyl and phenoxycarbonyl; hydrocarbylcarbonyl such as formyl, acetyl, and benzoyl; hydrocarbylcarbonyloxy such as acetoxy, benzoxy, and cyclohexanecarbonyloxy; hydrocarbylcarbonamido, e.g., acetamido, benzamido; azo, boryl; halo, e.g., chloro, iodo, bromo, and fluoro; hydroxy; cyano; nitro; nitroso, oxo; dimethylamino; diphenylphosphino, diphenylarsino; diphenylstibine; trimethylgermyl; tributylstannyl; methylseleno; ethyltelluro; and trimethylsiloxy; condensed rings such as benzo, cyclopenta; naphtho, indeno; and the like.

Each L^1 and L^2 in formula I is provided by monodentate and polydentate compounds preferably containing up to about 30 carbon atoms and up to 10 hetero atoms selected from nitrogen, sulfur, non-peroxidic oxygen, phosphorous, arsenic, selenium, antimony, and tellurium, whereupon addition to the metal atom, following loss of zero, one, or two hydrogens, the polydentate compounds preferably forming with the metal, M, a 4-, 5-, or 6-membered saturated or unsaturated ring. Examples of suitable monodentate compounds or groups are carbon monoxide, carbon sulfide, carbon selenide, carbon telluride, alcohols such as ethanol, butanol, and phenol; nitrosonium (i.e., NO^+); compounds of Group VA elements such as ammonia, phosphine, trimethylamine, trimethylphosphine, triphenylamine, triphenylphosphine, triphenylarsine, triphenylstibine, tributylphosphite, isonitriles such as phenylisonitrile, butylisonitrile; carbene groups such as ethoxymethylcarbene, dithiomethoxycarbene; alkylidenes such as methylidene, ethylidene; suitable polydentate compounds or groups include 1,2-bis(diphenylphosphino)ethane, 1,2-bis(diphenylarsino)ethane, bis(diphenylphosphino)methane, ethylenediamine, propylenediamine, diethylenetriamine, 1,3-diisocyanopropane, and hydridotripyrrazolylborate; the hydroxycarboxylic acids such as glycolic acid, lactic acid, salicylic acid; polyhydric phenols such as catechol and 2,2'-dihydroxybiphenyl; hydroxyamines such as ethanolamine, propanolamine, and 2-aminophenol; dithiocarbamates such as diethyldithiocarbamate, dibenzyldithiocarbamate; xanthates such as ethyl xanthate, phenyl xanthate; the dithiolenes such as bis(perfluoromethyl)-1,2-dithiolene; aminocarboxylic acids such as alanine, glycine and o-aminobenzoic acid; dicarboxylic diamines as oxalamide, biuret; diketones such as 2,4-pentanedione; hydroxyketones such as 2-hydroxyacetophenone; alpha-hydroxyoximes such as salicylaldoxime; ketoximes such as benzil oxime; and glyoximes such as dimethylglyoxime. Other suitable groups are the inorganic groups such as, for example, CN^-, SCN^-, F^-, OH^-, Cl^-, Br^-, I^-, and H^- and the organic groups such as, for example, acetoxy, formyloxy, benzoyloxy, etc. As mentioned before, the ligand can be a unit of a polymer, for example the amino group in poly(ethyleneamine); the phosphino group in poly(4-vinylphenyldiphenylphosphine); the carboxylic acid group in poly(acrylic acid); and the isonitrile group in poly(4-vinylphenylisonitrile).

Suitable ligands L^3 in formula I include any group having in its structure an atom with an unshared electron. Suitable groups can contain any number of carbon atoms and hetero atoms but preferably contain less than 30 carbon atoms and up to 10 hetero atoms selected from nitrogen, sulfur, oxygen, phosphorus, arsenic, selenium, antimony, tellurium, silicon, germanium, tin, and boron. Examples of such groups are hydrocarbyl groups such as methyl, ethyl, propyl, hexyl, dodecyl, phenyl, tolyl, etc.; unsaturated hydrocarbyl groups such as vinyl, eta¹-allyl, eta¹-butenyl, eta¹-cyclohexenyl; the hydrocarbyl derivatives of a Group IVA element such as trimethylgermyl, triphenylstannyl, trimethylsilyl, and triphenyllead, etc.; and organic groups such as formyl, acetyl, propionyl, acryloyl, octadecoyl, benzoyl, toluenesulfonyl, oxalyl, malonyl, o-phthaloyl.

Also suitable as L^3 is any group having in its structure two, three, or four unshared electrons, with the proviso that only one electron is shared per metal M. Examples of such groups are CH_2, $SiMe_2$, $SiPh_2$, $SnPh_2$, $GePh_2$, SiMe, SiPh, SnPh, Si, and Sn.

M can be any element from the Periodic Groups IVB, VB, VIB, VIIB, and VIIIB, such as, for example, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Pd and Pt.

In general, radiation-induced polymerization of ethylenically unsaturated monomers and one of polyurethane precursors and epoxy monomers with latent curing agents comprising an organometallic compound and an onium salt can be carried out at room temperature for the majority of energy curable compositions,

although low temperature (e.g., -10°C) or elevated temperature (e.g., 30 to 200°C, preferab[ly] ... 150°C) can be used to subdue the exotherm of polymerization or to accelerate the polymer[ization] respectively. Temperature of polymerization and amount of catalyst will vary and be dependent [on the] particular curable composition used and the desired application of the polymerized or cured produ[ct] ... amount of curing agent to be used in this invention should be sufficient to effect polymerization ... polymerizable mixtures (i.e., a catalytically-effective amount) under the desired use conditions. Such ... generally will be in the range of about 0.1 to 20 weight percent, and preferably 0.1 to 10.0 weight ... based on the weight of curable composition.

While not wishing to be bound by theory, we propose that when specified organometallic com[pounds] are irradiated in the presence of suitable oxidizing agents such as onium salts, intermediate comp[ounds] ... produced which can affect the curing of epoxides, urethanes, and vinyl monomers. It is believed ... transition metal-transition metal or metal-L^3 sigma bond cleaves homolytically upon photolysis. Ev[idence] ... this homolytic cleavage is provided for some organometallic compounds such as $[CpFe(CO)_2]_2$ ... $(CO)_{10}$ and involves the abstraction of Cl from CCl_4 subsequent to photolysis (G. Geoffroy ... Wrighton, "Organometallic Photochemistry," Academic Press, NY (1979), Chapters 2 and 8, par[t] ... 138). In other cases, spectroscopic data provides such evidence (O. Hackelberg, A. Wojcicki, In[org. Chim.] Acta 1980, 44, L63; R. G. Severson, A. Wojcicki, J. Organomet. Chem. 1978, ... The ... this bond homolysis then react with the oxidizing agent. By this process th... ...ytic spec[ies] ... polymerization of either the polyurethane precursors or epoxy monomers is derived from the orga[nometallic] compound, and, simultaneously the free radical initiator for the polymerization of the ethylenic[ally unsatu]rated monomers is derived from the oxidizing agent. In the limit cleavage of the sigma bond b[y] ... can ultimately lead to the production of two organometallic-derived species and two free radica[ls] ... should be noted that competing or secondary photo processes, such as dissociation of a car[bonyl] ... can occur. Such processes, however, occur in such a manner or to such an extent that ... catalytic species and initiator are still produced so as to effect curing of the composition.

Solvents, preferably organic can be used to assist in dissolution of the curing agent in the ... unsaturated monomer, and either polyurethane precursors or epoxy monomers, and as a pr[ocessing aid] ... Representative solvents include acetone, methyl ethyl ketone, cyclopentanone, methyl cell[osolve] ... methylene chloride, nitromethane, methyl formate, acetonitrile, gamma-butyrolactone, and ... [dimeth]yethane (glyme). In some applications, it may be advantageous to adsorb the curing agen[t onto an inert] support such as silica, alumina, clays, etc., as described in U.S. Patent No. 4,677,137.

For those compositions of the invention which are radiation-sensitive, i.e., the compo[sitions] ... ethylenically unsaturated monomers and either polyurethane precursors or epoxy monom[ers and as curing] agent a combination of an organometallic compound of Formula I and an onium salt, ... source of radiation including electron beam radiation and radiation sources emitting act[inic] ... ultraviolet and visible region of the spectrum (e.g., about 200 to 800 nm) can be used. S[uitable sources of] radiation include mercury vapor discharge lamps, carbon arcs, tungsten lamps, xen[on lamps] ... sunlight, etc. The required amount of exposure to effect polymerization is dependent up[on] ... the identity and concentrations of the organometallic compound and onium salt, the parti[cular ethylenically] unsaturated monomer, polyurethane precursors, and epoxy monomers, the thickness ... material, type of substrate, intensity of the radiation source and amount ...eat as[sociated with the] radiation.

Thermal polymerization using direct heating or infrared electromagnetic ra...n, as is ... can be used to cure ethylenically-unsaturated monomers and either polyurethane pr[ecursors or epoxy] monomers according to he teachings of this invention.

It is within the scope of this invention to include two-stage polymerization (curing), by ... curing agent by irradiating the curable compositions and subsequently thermally curing ... precursor so obtained, the irradiation temperature being below the temperature employed ... quent heat-curing. These activated precursors may normally be cured at temperatures whi[ch are substan]tially lower than those required for the direct thermal curing, with an advantage in the ra[nge ...] 110°C. This two-stage curing also makes it possible to control the polymerization in a par[ticularly simple] and advantageous manner.

Adjuvants such as solvents, pigments, abrasive granules, stabilizers, light stabilizers, a[ntioxidants, flow] agents, bodying agents, flatting agents, colorants, inert fillers, binders, blowing agents, f[ungicides, bac]teriocides, surfactants, plasticizers, and other additives as known to those skilled in the art c[an be added to] the compositions of this invention. These can be added in an amount effective for their inten[ded purpose.]

Compositions of this invention are useful for coatings, foams, shaped articles, adh[esives, filled or] reinforced composites, abrasives, caulking and sealing compounds, casting and mold[ing compounds] ...

although low temperature (e.g., -10°C) or elevated temperature (e.g. 30 to 200°C preferably 50 to 150°C) can be used to subdue the exotherm of polymerization or to accelerate the polymerization respectively. Temperature of polymerization and amount of catalyst will vary and be dependent on the particular curable composition used and the desired application of the polymerized or cured product. The amount of curing agent to be used in this invention should be sufficient to effect polymerization of the polymerizable mixtures (i.e., a catalytically-effective amount) under the desired use conditions. Such amount generally will be in the range of about 0.1 to 20 weight percent, and preferably 0.1 to 10.0 weight percent, based on the weight of curable composition.

While not wishing to be bound by theory, we propose that when specified organometallic compounds are irradiated in the presence of suitable oxidizing agents such as onium salts, intermediate compounds are produced which can affect the curing of epoxides, urethanes, and vinyl monomers. It is believed that the transition metal-transition metal or metal-L³ sigma bond cleaves homolytically upon photolysis. Evidence for this homolytic cleavage is provided for some organometallic compounds such as [CpFe(CO)₂]₂ and Mn₂(CO)₁₀ and involves the abstraction of Cl from CCl₄ subsequent to photolysis (G. Geoffrey and M Wrighton, "Organometallic Photochemistry," Academic Press, NY (1979), Chapters 2 and 8, particularly p 138). In other cases, spectroscopic data provides such evidence (O Hackelberg, A Wojcicki Inorg. Chem. Acta 1980, 44, L63; R G Severson, A Wojcicki J. Organomet. Chem. 1978, 157, 173). The product(s) of this bond homolysis then react with the oxidizing agent. By this process, the catalytic species for the polymerization of either the polyurethane precursors or epoxy monomers is derived from the organometallic compound, and, simultaneously the free radical initiator for the polymerization of the ethylenically unsaturated monomers is derived from the oxidizing agent. In the limit, cleavage of the sigma bond by one photon can ultimately lead to the production of two organometallic-derived species and two free radical initiators. It should be noted that competing or secondary photo processes, such as dissociation of a carbonyl ligand, can occur. Such processes, however, occur in such a manner or to such an extent that the effective catalytic species and initiator are still produced so as to effect curing of the composition.

Solvents, preferably organic can be used to assist in dissolution of the curing agent in the ethylenically-unsaturated monomer, and either polyurethane precursors or epoxy monomers, and as a processing aid. Representative solvents include acetone, methyl ethyl ketone, cyclopentanone, methyl cellosolve acetate, methylene chloride, nitromethane, methyl formate, acetonitrile, gamma-butyrolactone, and 1,2-dimethoxyethane (glyme). In some applications, it may be advantageous to adsorb the curing agent onto an inert support such as silica, alumina, clays, etc., as described in U.S. Patent No. 4,677,137.

For those compositions of the invention which are radiation-sensitive, i.e., the compositions containing ethylenically unsaturated monomers and either polyurethane precursors or epoxy monomers and as curing agent a combination of an organometallic compound of Formula I and an onium salt of Formula II, any source of radiation including electron beam radiation and radiation sources emitting active radiation in the ultraviolet and visible region of the spectrum (e.g., about 200 to 800 nm) can be used. Suitable sources of radiation include mercury vapor discharge lamps, carbon arcs, tungsten lamps, xenon lamps, lasers, sunlight, etc. The required amount of exposure to effect polymerization is dependent upon such factors as the identity and concentrations of the organometallic compound and onium salt, the particular ethylenically unsaturated monomer, polyurethane precursors, and epoxy monomers, the thickness of the exposed material, type of substrate, intensity of the radiation source and amount of heat associated with the radiation.

Thermal polymerization using direct heating or infrared electromagnetic radiation, as is known in the art, can be used to cure ethylenically-unsaturated monomers and either polyurethane precursors or epoxy monomers according to the teachings of this invention.

It is within the scope of this invention to include two-stage polymerization (curing), by first activating curing agent by irradiating the curable compositions and subsequently thermally curing the activated precursor so obtained, the irradiation temperature being below the temperature employed for the subsequent heat-curing. These activated precursors may normally be cured at temperatures which are substantially lower than those required for the direct thermal curing, with an advantage in the range from 50 to 110°C. This two-stage curing also makes it possible to control the polymerization in a particularly simple and advantageous manner.

Adjuvants such as solvents, pigments, abrasive granules, stabilizers, light stabilizers, antioxidants, flow agents, bodying agents, flatting agents, colorants, inert fillers, binders, blowing agents, fungicides, bacteriocides, surfactants, plasticizers, and other additives as known to those skilled in the art can be added to the compositions of this invention. These can be added in an amount effective for their intended purpose.

Compositions of this invention are useful for coatings, foams, shaped articles, adhesives, filled or reinforced composites, abrasives, caulking and sealing compounds, casting and molding compounds,

ENERGY-INDUCED DUAL CURABLE COM

FIELD OF THE INVENTION

This invention relates to an energy-polymerizable composi monomer and either polyurethane precursors or an epoxy mi an organometallic compound and an oxidizing agent and a articles comprising the composition of the invention are example, as protective coatings, binders for magnetic media applications.

Background Of The Invention

Various polymeric coatings and article roduc solvents. There is an intense effort by law resear solids formulations to reduce or eliminate the use of such s tal contamination. These processes require a latent cata activated in a controlled fashion.

Thermal curing of polyurethane precursors using tiaryamines is known in the art. Curing of polymerizable to as polyurethane precursors) using thermally latent cata Patent Nos. 4,521,545, and 4,582,861).

Photocuring of urethane (meth)acrylates is well kno S.Y. Tsay, M. Koshiba, Y.S. Ding, S.L. Cooper J. Appl. Polym.-Plast. Technol. Eng. 1981, 17, 83-93), and phot salts, tertiaryamine precursors, and organotin compou 4,549,945, and EP 28,696 Derwent abstract). All of the disadvantages: sensitivity to oxygen, requirement modified resins, loss or dilution of urethane properties.

The dual curing of acrylate urethane precursor entirely photoactivated nor are any methods known precursors and acrylates (see U.S. Pat. 4,342,793; pages 48-55).

The prior art discloses processes for the polym metallocene, such as ferrocene, can be used as a 3,705,129). U.S. Patent Nos. 3,709,861, 3,714,006 metal complexes in the reaction between polyepox teach the polymerization of epoxide gro polymerization of epoxide group-contain which the polymerization catalyst is a radia sensit is described in U.S. Patent No. 3,794,576 and U.S. Pat U.S. Patent No. 4,026,705 and the onium salts of Grou are disclosed in U.S. Patent No. 4,058,400), or a dicarb as is disclosed in U.S. Patent No. 4,086,091. These polymerization. Furthermore the dicarbonyl chelates are

U.S. Patent No. 4,216,288 teaches the thermal curing onium salts and reducing agents.

Radiation dual curable compositions containing eth omers have been described in U.S. Patent Nos. 4,156 include onium salts combined with organic compound organometallic compounds.

Energy polymerizable compositions comprising cationically sensitive materials and the curing thereof Nos. 109,851, 1984 Derwent abstract, 094,915, 1983 abstract).

potting and encapsulated compounds, impregnating and coating compounds, and other applications which are known to those skilled in the art.

Compositions of this invention may be applied, preferably as a liquid, to a substrate such as steel, aluminum, copper, cadmium, zinc, glass, paper, wood, or variou plastic films such as poly(ethylene terephthalate), plasticized p ly(vinylchloride), poly(propylene), poly(ethylene), and the like, and irradiated. By polymerizing part of the coating, as by irradiation through a mask, those sections which have not been exposed may be washed with a solvent to remove the unpolymerized portions while leaving the photopolymerized, insoluble portions in place. Thus, compositions of this invention may be used in the production of articles useful in the graphic arts such as printing plates and printed circuits. Methods of producing printing plates and printed circuits from photopolymerizing compositions are well known in the art (see for example British Patent Specification No. 1,495,746).

Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention. In the examples, all parts are parts by weight unless indicated otherwise. All examples were prepared in ambient atmosphere (presence of oxygen and water) unless indicated otherwise. In the examples:

Me = methyl

Ph = phenyl

Cp = cyclopentadienyl

EXAMPLE 1

The organometallic compounds, $[CpFe(CO)_2]_2$, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$ and $[CpMo(CO)_3]_2$ were obtained from Pressure Chemical Company and used without further purification. The other compounds were prepared using standard organometallic synthetic techniques. The procedure used will be illustrated for the preparation of $CpFe(CO)_2SnPh_3$.

The anion, $CpFe(CO)_2^-$, was produced by reducing 3.0g of $[CpFe(CO)_2]_2$ with 0.41g of sodium and 0.59g of benzophenone in 200 mL of freshly distilled tetrahydrofuran under an atmosphere of argon. The reaction was allowed to proceed for about 24 hours by which time the starting material had all been reduced to the anion as indicated by infrared spectroscopy (IR). To the solution of the anion was added, under argon, 6.5 g of $ClSnPh_3$ as a solid. The reaction was stirred until the anion was consumed as shown by IR. The reaction vessel was opened to air and the solvent removed under reduced pressure. The solid residue was taken up in methylene chloride and passed down a short silica gel column. Crystals were obtained by removing the methylene chloride under reduced pressure and adding hep .e. The product was identified by IR, nuclear magnetic resonance spectroscopy (NMR), elemental an., .s and melting point. In a similar manner all the other materials in Table I were prepared.

These compounds are used in subsequent examples.

TABLE I

Characterization of Compounds			
Compound	Elemental Analysis (Report/Calculated)		Melting Point (°C)
	%C	% H	
$CpFe(CO)_2SnPh_3$	57.0/57.0	3.8/3.8	136-138
$CpFe(CO)_2GePh_3$	62.3/62.4	4.2/4.2	159-160
$CpFe(CO)_2PbPh_3$			
$[CpFe(CO)_2]_2SnPh_2$	48.7/48.8	3.3/3.2	146-149
$(CO)_5MnSnPh_3$	51.0/50.7	2.8/2.8	146-149
$(CO)_5MnPbPh_3$			
$[(CO)_5Mn]_2SnPh_2$	39.9/39.8	1.8/1.5	138-139
$(CO)_5ReSnPh_3$			
$CpMoSnPh_3$	52.8/52.5	3.4/3.4	213-214

EXAMPLE 2

Several organometallic compounds were prepared according to literature methods. $CpW(CO)_3(CH_3)$ prepared according to the method of T S. Piper, G. Wilkinson, Inorg. Nucl. Chem., 1956, 3, 104-124. ... $(CO)_3]_2$ was prepared according to the method of R. Birdwhistell, P. Hackett, A. R. Manning, J. Organ... Chem., 1978, 157, 239. $CpFe(CO)_2SiPh_3$ was prepared according to the method of G. Cerveau, E. Co... R. Corriu, W. E. Douglas, J. Organomet. Chem., 1977, 135, 373, 388. The method of J. P. ... Wojcicki, J. Amer. Chem. Soc., 1966, 88, 4862 was used to prepare $CpFe(CO)_2(CPh_3)$, and that of King, M. B. Bisnette, J. Organomet. Chem., 1964, 2, 15-37, to prepare $CpFe(CO)_2COPh$. The prep... of $CpPtMe_3$ has been described in U.S. Patent No. 4,600,484.

These compounds are used in subsequent examples.

EXAMPLE 3 (Comparative)

This example illustrates the use of an organometallic compound containing a transition metal-... metal single bond in the curing agent to photocatalyze the formation of polyure... stock s... 8.02 g 4,4'-methylenebis(cyclohexylisocyanate) (Desmodur™ W, a Mobay Corp., ...gh, PA) a... g polyethylene glycol MW400 (Carbowax™ 400, Union Carbide, Danbury, CT) was prepared. To a... of 0.01 g $[CpFe(CO)_2]_2$ and 0.02 g $Ph_2I^+ PF_6^-$ in 0.1 g gamma-butyrolactone was added 1.25... stock solution. The sample was photocured to a solid using a Kodak™ Carousel™ projector in 12...

Three samples were prepared as above, except the iron dimer and iodonium salt were ... follows: sample (a), 0.01 g $[CpFe(CO)_2]_2$, 0.03 g $Ph_2I^+ PF_6^-$; sample (b), 0.01 g $[CpFe(CO)_2]_2$, ... 0.03 g $Ph_2I^+ PF_6^-$. (a) was left in the dark while samples (b) and (c) were irradiated as above. N... three samples showed evidence of any curing, no obvious change in viscosity as evidence... minutes.

EXAMPLE 4 (Comparative)

This example illustrates the use of an organometallic compound containing a transitio... single bond in the curing agent to photocatalyze the formation of polyurethane. 0.52 g Desm... methylene bis (cyclohexyl isocyanate)) and 0.72 g Carbowax 400 (polyol) were combined a... 0.01 g $CpPt(CH_3)_3$ (Cp = eta^5-cyclopentadienyl) which had been dissolved in ca. 0.15 m... CH_2Cl_2 and gamma-butyrolactone. The resulting mixture was irradiated with a Hanovia™ 45... pressure mercury arc lamp through Pyrex™. Complete cure was achieved within 12 mi... time.

EXAMPLE 5

This example describes the photocuring of Henkel Duo-Cure™ (Henkel Corp., Minneapolis, ... multifunctional acryl... The Henkel Duo-Cure™ resins are polyol/aliphatic polyisocyanate and multifunctional acr... containing no curing agents. The resins are dual curing resins, and are claimed to form inter... networks (IPN's) when properly cured.

Samples were prepared, 2.0 g in size, using 77 parts Henkel Duo-Cure 172A, 23 parts Duo... 0.5 parts $[CpFe(CO)_2]_2$, and 1 part $Ph_2I^+ PF_6^-$. One sample was cured in the vial using a s... cured in <3.0 minutes to a clear, hard mass. The other sample was coated on a tongue de... exposed to the suntan lamp. Curing occurred in 15 seconds, to yield a clear, hard, sandа... Infrared spectra of thin coatings on salt plates showed conversion of the isocyanate to ur... exposure to sunlamp radiation.

EXAMPLE 2

Several organometallic compounds were prepared according to literature methods $CpW(CO)_3(CH_3)$ was prepared according to the method of T S Piper, G. Wilkinson, Inorg Nucl Chem, 1956, 3, 104-124 [CpW-$(CO)_3]_2$ was prepared according to the method of R Birdwhistell P Hackett, A R Manning, J Organomet Chem., 1978, 157, 239 $CpFe(CO)_2SiPh_3$ was prepared according to the method of G Cerveau, E Colomer, R Corriu, W E Douglas, J Organomet. Chem., 1977, 135, 373, 388 The method of J P Bibler, A Wojcicki, J Amer Chem Soc., 1966, 88, 4862 was used to prepare $CpFe(CO)_2(CPh_3)$, and that of R B King, M B Bisnette, J Organomet Chem., 1964, 2, 15-37, to prepare $CpFe(CO)_2COPh$. The preparation of $CpPtMe_3$ has been described in U S. Patent No 4,600,484

These compounds are used in subsequent examples

EXAMPLE 3 (Comparative)

This example illustrates the use of an organometallic compound containing a transition metal-transition metal single bond in the curing agent to photocatalyze the formation of polyurethane. A stock solution of 8.02 g 4,4'-methylenebis(cyclohexylisocyanate) (Desmodur™ W, a Mobay Corp., Pittsburgh, PA) and 11.20 g polyethylene glycol MW400 (Carbowax™ 400, Union Carbide, Danbury, CT) was prepared. To a solution of 0.01 g $[CpFe(CO)_2]_2$ and 0.02 g Ph_2I^+ PF_6^- in 0.1 g gamma-butyrolactone was added 1.25 g of the stock solution The sample was photocured to a solid using a Kodak™ Carousel™ projector in 12 minutes.

Three samples were prepared as above, except the iron dimer and iodonium salt were added as follows sample (a), 0.01 g $[CpFe(CO)_2]_2$, 0.03 g Ph_2I^+ PF_6^-, sample (b), 0.01 g $[CpFe(CO)_2]_2$, sample (c), 0.03 g Ph_2I^+ PF_6^-. (a) was left in the dark while samples (b) and (c) were irradiated as above None of the three samples showed evidence of any curing, no obvious change in viscosity as evidence, after 20 minutes

EXAMPLE 4 (Comparative)

This example illustrates the use of an organometallic compound containing a transition metal-carbon single bond in the curing agent to photocatalyze the formation of polyurethane 0.52 g Desmodur W (4,4'-methylene bis (cyclohexyl isocyanate)) and 0.72 g Carbowax 400 (polyol) were combined and added to ca. 0.01 g $CpPt(CH_3)_3$ (Cp = eta^5-cyclopentadienyl) which had been dissolved in ca 0.15 ml of a mixture of CH_2Cl_2 and gamma-butyrolactone The resulting mixture was irradiated with a Hanovia™ 450 watt medium pressure mercury arc lamp through Pyrex™ Complete cure was achieved within 12 minutes irradiation time

EXAMPLE 5

This example describes the photocuring of Henkel Duo-Cure™ (Henkel Corp., Minneapolis, MN) resins The Henkel Duo-Cure™ resins are polyol-aliphatic polyisocyanate and multifunctional acrylate systems containing no curing agents. The resins are dual curing resins, and are claimed to form interpenetrating networks (IPN's) when properly cured

Samples were prepared, 2.0 g in size, using 77 parts Henkel Duo-Cure 172A, 23 parts Duo-Cure 172B, 0.5 parts $[CpFe(CO)_2]_2$, and 1 part Ph_2I^+ PF_6^-. One sample was cured in the vial using a suntan lamp, cured in <3.0 minutes to a clear, hard mass The other sample was coated on a tongue depressor and exposed to the suntan lamp Curing occurred in 15 seconds, to yield a clear, hard, sandable coating Infrared spectra of thin coatings on salt plates showed conversion of the isocyanate to urethane upon exposure to suntamp radiation

EXAMPLE 6 (Comparative)

This example illustrates the photocuring of polyurethane precursors to polyurethanes in the presence and absence of O_2 using transition metal-transition metal bond containing organometallic compounds and onium salt as curing agent.

A mixture of 10 mg $[CpFe(CO)_2]_2$, 30 mg $Ph_2I^+ PF_6^-$, 0.1 g gamma-butyrolactone, 0.83 g Desmodur™ W (4,4'-methylenebis(cyclohexylisocyanate)), and 1.17 g polyethyleneglycol (MW = 400) was divided in half. One half was bubbled with N_2 for 2-3 minutes, the other left open to the atmosphere. Both samples were irradiated simultaneously with the output of a 450 watt Hanovia mercury lamp, filtered through Pyrex and a water infrared filter. Both samples cured after 10.0 minutes irradiation. This demonstrates that in the presence of onium salt, curing occurs with or without O_2 present.

EXAMPLE 7 (Comparative)

This example describes the photocuring of polyurethane precursors using transition metal containing organometallic compounds and iodonium and sulfonium salts. A stock solution was prepared from 7 parts Desmodur W, 1.9 parts butanediol, and 0.5 parts trimethylolpropane. Samples were prepared as in Example 3 using 1.25 g of the stock solution, 0.01 g neutral metal-metal bonded compound and 0.015 g $Ph_2I^+ PF_6^-$ in 0.05 g gamma-butyrolactone. Irradiations were carried out on a 450 W Hanovia medium pressure mercury arc through Pyrex. Alternatively, these compositions can be cured thermally.

TABLE II

Iodonium and Sulfonium Salts		
Organometallic Compound	Cure time, minutes	
	$Ph_2I^+ PF_6^-$	$Ph_3S^+ PF_6^-$
$[Co(CO)_4]_2$	6.0	>100
$[CpFe(CO)_2]_2$	9.0	20-25
$[Mn(CO)_5]_2$	12-20	7-12
$[Re(CO)_5]_2$	20-40	20-40
$Co_4(CO)_{12}$	40-55	55-66
$[CpMo(CO)_3]_2$	55-67	60-[illegible]
$Fe_2(CO)_9$	ca. 60	--

EXAMPLE 8 (Comparative)

This provides further examples of bicomponent curing agents wherein organometallic compounds contain transition metal-carbon bonds which are effective in the curing agent for polyurethane precursors. A stock solution of polyurethane precursors was prepared by mixing 23.1 g Desmodur W and 32.6 g Carbowax 400 and shaking well before use. Samples were prepared by dissolving 10 mg catalyst and 20 mg diphenyliodonium hexafluorophosphate (if used) in 0.2 g CH_2Cl_2. 2.0 g stock solution was added in the dark, and samples were then irradiated under a Hanovia Quartz Utility Lamp. The temperature of samples under the lamp reached ca. 50°C within 10 min. The time to a viscocity increase is noted in Table III, and "cure time" is the time for a sample to become so viscous that it would not flow. "Partial cure" is indicated when, within 30 min irradiation, the sample became more viscous but would still flow.

TABLE III

Curing of Polyurethane Precursors		
	Cure Rates, min	
	Viscosity Increase	Cured
$CpPtMe_3$	7	30
$CpPtMe_3$ + iodonium	7	30
$CpW(CO)_3Me$	30	partial
$CpW(CO)_3Me$ + iodonium	30	partial
$[(PMe_2Ph)_2PtMe_3(acetone)]^+PF_6^{-a}$	13	partial
$[CpFe(CO)_2]_2$ + iodonium[a]	9	30

a included for purposes of comparison

The data show curing occurs with or without iodonium salts. In some cases, adventitious oxyge provide a suitable oxidizing agent. However, the use of onium salts is preferred since it is much ea control the organometallic oxidizing agent ratio.

EXAMPLE 9 (Comparative)

This example describes the use of the curing agent containing an organometallic compound c a transition metal-carbon bond to cure epoxies. Each sample was prepared by dissolving 10 mg in 0.2 g CH_2Cl_2, 2.0 g cyclohexene and 20 mg diphenyliodonium hexafluorophosphate (if used) under a Hanovia Quartz Utility lamp. Initial added in the dark, and samples were then irradiated under a Hanovia Quartz Utility lamp. Formation of polymer was tested by placing a few drops of the sample in about 2 mL methanol. Formation indicated that polymer had formed. Further polymerization resulted in a viscocity increase in Results are indicated in Table IV.

TABLE IV

Curing Agent	Precipitate formed, min	Viscosity increased, min.
$CpPtMe_3$	no cure	no cure
$CpPtMe_3$ + iodonium	3.5	
$CpW(CO)_3Me$ + iodonium	3	
$(PMe_2Ph)_2PtMe_3(acetone)]^+PF_6^{-a}$	2	no further cure
$[CpFe(CO)_2]_2$ + iodonium[a]	2	30

a included for propose of comparison.

EXAMPLE 10 (Comparative)

Examples of the ability of curing agent containing transition metal-transition metal bonded type organometallic compounds and onium salt to photoinitiate the cure of epoxies are provided tests were carried out in the following manner: into a glass vial were weighed out 0.10g of organic metallic compound and/or 0.20g diphenyliodonium hexafluorophosphate (3M Company, rec from acetone/isopropanol). Then, the following operations were carried out under subdued lig gamma-butyrolactone, 2.0g cyclohexene oxide (Aldrich Chemical Company, distilled), 8.0g epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (ERL-4221, Union Carbide Company

... ...thanes in the presence ...metallic compounds and

...one 0.83 g Desmodur™ ...(MW = 400) was divided in ... atmosphere. Both samples ...amp filtered through Pyrex ... demonstrates that in the

...ing transition metal containing ...ion was prepared from 7 parts ...s were prepared as in Example ...und and 0.015 g $Ph_3I^+ PF_6^-$ ...W Hanovia medium pressure ...thermally.

...wherein organometallic compounds ...agent for polyurethane precursors A ...3 g Desmodur W and 32.6 g ...dissolving 10 mg catalyst and 20 ...g stock solution was added in the ...lamp. The temperature of samples ...increase is noted in Table III, and ...llow. "Partial cure" is indicated ...st flow.

TABLE III

Curing of Polyurethane Precursors	Cure Rates, min	
	Viscosity Increase	Cured
$CpPtMe_3$	7	30
$CpPtMe_3$ + iodonium	7	30
$CpW(CO)_3Me$	30	partial
$CpW(CO)_3Me$ + iodonium	30	partial
$[(PMe_2Ph)_2PtMe_3(acetone)]^+PF_6^{-a}$	13	partial
$[CpFe(CO)_2]_2$ + iodonium^a	9	30

a included for purposes of comparison

The data show curing occurs with or without iodonium salts. In some cases, adventitious oxygen can provide a suitable oxidizing agent. However, the use of onium salts is preferred since it is much easier to control the organometallic oxidizing agent ratio.

EXAMPLE 9 (Comparative)

This example describes the use of the curing agent containing an organometallic compound containing a transition metal-carbon bond to cure epoxies. Each sample was prepared by dissolving 10 mg catalyst and 20 mg diphenyliodonium hexafluorophosphate (if used) in 0.2 g CH_2Cl_2. 2.0 g cyclohexene oxide was added in the dark, and samples were then irradiated under a Hanovia Quartz Utility lamp. Initial formation of polymer was tested by placing a few drops of the sample in about 2 mL methanol. Formation of precipitate indicated that polymer had formed. Further polymerization resulted in a viscocity increase in the sample. Results are indicated in Table IV

TABLE IV

Curing Agent	Precipitate formed, min	Viscosity increased, min.
$CpPtMe_3$	no cure	no cure
$CpPtMe_3$ + iodonium	3.5	30
$CpW(CO)_3Me$ + iodonium	3	30
$(PMe_2Ph)_2PtMe_3(acetone)]^+PF_6^{-a}$	2	no further cure
$[CpFe(CO)_2]_2$ + iodonium^a	2	30

a included for proposes of comparison.

EXAMPLE 10 (Comparative)

Examples of the ability of curing agent containing transition metal-transition metal bonded and M-L³ type organometallic compounds and onium salt to photoinitiate the cure of epoxies are provided here. The tests were carried out in the following manner: Into a glass vial were weighed out 0.10g of the desired organic metallic compound and/or 0.20g diphenyliodonium hexafluorophosphate (3M Company, recrystallized from acetone-isopropanol). Then, the following operations were carried out under subdued light. 0.3g of gamma-butyrolactone, 2.0g cyclohexene oxide (Aldrich Chemical Company, distilled), 5.0g of 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (ERL-4221, Union Carbide Company) were ad-

$[(CO)_5Mn]_2SnPh_2$
$CpFe(CO)_2PbPh_3$
$(CO)_5MnPbPh_3$
$(CO)_5ReSnPh_3$
$CpPtMe_3$
$CpW(CO)_3Me$
$Cp(CO)_3W\text{-}Mo(CO)_3Cp$
$Cp(CO)_3Mo\text{-}Mn(CO)_5$
$Cp(CO)_3Mo\text{-}Re(CO)_5$
$Cp(CO)_3W\text{-}Mn(CO)_5$
$Cp(CO)_3W\text{-}Re(CO)_5$
$Cp(CO)_3Mo\text{-}Co(CO)_4$
$Cp(CO)_3W\text{-}Co(CO)_4$
$Cp(CO)_3Mo\text{-}Fe(CO)_2Cp$
$(CO)_5Mn\text{-}Fe(CO)_2Cp$
$Cp(CO)_3W\text{-}Fe(CO)_2Cp$
$[CpMo(CO)_2PPh_3]_2$
$Mn_2(CO)_9PPh_3$
$Mn_2(CO)_8(PPh_3)_2$
$(CO)_5Mn\text{-}Re(CO)_5$
$Mn_2(CO)_8$ (1,10-phenanthroline)
$[CpFe(CO)_2]_4Si$
$Re_2(CO)_8$(1,10-phenanthroline)
$Re_2(CO)_8$(2,2'-biquinoline)
$Fe_3(CO)_{12}$
$Ru_3(CO)_{12}$
$Os_3(CO)_{12}$
$Ru_3(CO)_{11}PPh_3$
$Ru_3(CO)_{10}(Ph_2P\text{-}CH_2CH_2\text{-}PPh_2)$
$Fe_2Ru(CO)_{12}$
$Ir_4(CO)_{12}$
$[CpNi(CO)]_2$
$CpFe(CO)_2CH_2Ph$
$CpFe(CO)_2(COPh)$
$CpFe(CO)_2(SiPh_3)$
$[Cp^* Fe(CO)_2]_2$
$Cp(CO)_2Fe\text{-}Fe(CO)(PPh_3)Cp$
$(MeCp)PtMe_3$
$(Me_3SiCp)PtMe_3$
$Cp(CO)_3Mo\text{-}Mo(CO)_2(PPh_3)Cp$
wherein
Me is methyl
Ph is phenyl
Cp is eta⁵-cyclopentadienyl
Cp* is eta⁵-pentamethylcyclopentadienyl

A wide variety of monomers can be energy polymeriz... Suitable compounds containing at least one ethylenically-un... and/or oligomers such as (meth)acrylates, (meth)acrylamides... undergoing addition polymerization. Such monomers inc... methacrylates such as methyl acrylate, methyl methacrylate, ... acrylate, stearyl acrylate, allyl acrylate, glycerol diacrylate, ... diethyleneglycol diacrylate, triethyleneglycol dimethacrylate, ... dimethacrylate, trimethylolpropane triacrylate, 1,2,4-butanetrio... crylate, pentaerythritol triacrylate, pentaerythritol tetraacrylat... hexacrylate, bis[1-(2-acryloxy)]-p-ethoxyphenyldimethylm... propoxyphenyl-dimethylmethane, tris-hydroxyethyl-isocyanurate... methacrylates of polyethylene glycols of molecular weight 20... monomers such as those of U.S. Patent No. 4,652,274, and

ded to prepare the coating solution. The solutions were coated onto 76 micrometers (3 mil) polyvinylidene chloride subbed polyester (3M Company) using a #22 wire wound rod. The sample coatings were exposed in air, to a 275 watt G.E. sunlamp at a distance of 10cm. The time to "set to cotton" is recorded in Table V, that is the time needed to cure the coating so that when it is touched with a cotton ball, it leaves no smear or picks up no cotton threads. This test establishes the time required to cure the coating. Under the conditions of this test, the diphenyliodonium hexafluorophosphate alone requires greater than 10 min to cure.

TABLE V

Photoinitiation of Epoxy Cure		
Compound	Cure Time[a]	
	No Onium Salt Added	Onium Salt Added
$[CpFe(CO)_2]_2$	>10	1
$CpFe(CO)_2SnPh_3$	>10	5
$CpFe(CO)_2GePh_3$	>10	5
$[CpFe(CO)_2]_2SnPh_2$	>10	3
$Mn_2(CO)_{10}$	>10	1
$(CO)_5MnSnPh_3$	>10	4
$[(CO)_5Mn]_2SnPh_2$	>10	3
$Re_2(CO)_{10}$	1	1.5
$CpMo(CO)_3SnPh_3$	8	4

a time in minutes to cure

EXAMPLE 11 (Comparative)

To further demonstrate the activity of the curing agent, a series of experiments were carried out in another epoxy and/or acrylate composition. The organometallic compound, with and without the onium salt, was photolyzed in presence of an epoxy or acrylate. The specific system used is as follows: methyl acrylate was distilled from hydroquinone and stored cold until ready for use. Cyclohexene oxide was used as obtained from Aldrich. The organometallic compounds were obtained from commercial sources. Diphenyliodonium hexafluorophosphate was recrystallized from acetone/isopropanol. All experiments were done as 100% solids except as noted.

In a small vial was placed 0.02 g of the organometallic compound with/without 0.04 g of the iodonium salt along with 2 g of the desired monomer. For the acrylate tests, the solutions were purged with N_2 for 60 sec before and continuously during the photolysis. The epoxy tests were performed without purging; vials open to the air. The light source was one 15 watt daylight fluorescent bulb. In Table VI below, the cure times represent the time required to reach the same degree of cure, usually gelation of the solution. Alternatively, the acrylate compositions can be cured thermally.

TABLE VI

Photoinitiated Cure Times of Epoxy and Acrylate Compositions[a]		
Catalyst System	Epoxy	Acrylate
$[CpFe(CO)_2]_2$	>900	>600
$[CpFe(CO)_2]_2$ iodonium	60	10
$Mn_2(CO)_{10}$	>900	>600
$Mn_2(CO)_{10}$ iodonium	200	45
$Re_2(CO)_{10}$	>900	360
$Re_2(CO)_{10}$ iodonium	200	60
$Co_2(CO)_8$	b	b
$Co_2(CO)_8$ iodonium	c	200
$Co_4(CO)_{12}$	b	b
$Co_4(CO)_{12}$ iodonium[d]	>900	60
iodonium	>900	>300

a Cure time in seconds
b Not done
c Reacted in the dark upon mixing
d 10% by wt. gamma-butyrolactone added

EXAMPLE 12 (Comparative)

This example demonstrates the ability of transition metal-transition metal [illegible] ganometallic compounds to photoinitiate the cure of ethylenically-unsaturated [illegible] of iodonium salts. The tests were carried out in the following manner: into a glass [illegible] 0.05g of the desired organometallic compound and 0.10g diphenyliodonium [illegible] Company, recrystallized from acetone/isopropanol. Then the following [illegible] subdued light: 0.2g of gamma-butyrolactone, 5.0g methyl acrylate (Aldrich [illegible] from hydroquinone), 5.0g of pentaerythritol tetraacrylate (SR-295, Sartomer [illegible] prepare the coating solution. The solutions were coated onto 76 micrometers [illegible] subbed polyester (3M Company) using a #22 wire wound rod. The sample [illegible] second sheet of polyester and exposed to two 15 watt Sylvania blacklight [illegible] time required to produce a nontacky cured coating was recorded. Under the [illegible] diphenyliodonium hexafluorophosphate alone requires greater than 15 min [illegible]

TABLE VI

Photoinitiated Cure Times of Epoxy and Acrylate Compositions[a]		
Catalyst System	Epoxy	Acrylate
$[CpFe(CO)_2]_2$	>800	>600
$[CpFe(CO)_2]_2$ iodonium	60	30
$Mn_2(CO)_{10}$	>800	>600
$Mn_2(CO)_{10}$ iodonium	200	45
$Re_2(CO)_{10}$	>800	380
$Re_2(CO)_{10}$ iodonium	200	60
$Co_2(CO)_8$	b	b
$Co_2(CO)_8$ iodonium	c	200
$Co_4(CO)_{12}$	b	b
$Co_4(CO)_{12}$ iodonium[d]	>900	80
iodonium	>900	>300

a Cure time in seconds
b Not done
c Reacted in the dark upon mixing
d 10% by wt gamma-butyrolactone added

EXAMPLE 12 (Comparative)

This example demonstrates the ability of transition metal-transition metal bonded or ML type organometallic compounds to photoinitiate the cure of ethylenically-unsaturated compounds in the presence of iodonium salts. The tests were carried out in the following manner. Into a glass vial were weighed out 0.05g of the desired organometallic compound and/or 0.10g diphenyliodonium hexafluorophosphate (3M Company, recrystallized from acetone/isopropanol). Then the following operations were carried out under subdued light: 0.2g of gamma-butyrolactone, 5.0g methyl acrylate (Aldrich Chemical Company, distilled from hydroquinone), 5.0g of pentaerythritol tetraacrylate (SR-295, Sartomer Company) were added to prepare the coating solution. The solutions were coated onto 76 micrometers (3 mil) polyvinylidene chloride subbed polyester (3M Company) using a #22 wire wound rod. The sample coatings were overlayed with a second sheet of polyester and exposed to two 15 watt Sylvania blacklight bulbs at a distance of 2 cm. The time required to produce a nontacky cured coating was recorded. Under the conditions of this test, the diphenyliodonium hexafluorophosphate alone requires greater than 15 min to cure.

TABLE VII

Curing of Ethylenically Unsaturated Monomers		
Organometallic Compound	Cure Time[a]	
	No Onium Salt Added	Onium Salt Added
$[CpFe(CO)_2]_2$	>600	15
$CpFe(CO)_2SnPh_3$	>600	120
$CpFe(CO)_2GePh_3$	>600	120
$[CpFe(CO)_2]_2SnPh_2$	>600	60
$Mn_2(CO)_{10}$	>600	<15
$(CO)_5MnSnPh_3$	300	300
$[(CO)_5Mn]_2SnPh_2$	60	30
$Re_2(CO)_{10}$	120	60
$[CpMo(CO)_3]_2$[b]	>600	30
$CpMo(CO)_3SnPh_3$	>600	240

a time in seconds to cure
b saturated solution <0.01g dissolved

EXAMPLE 13 (Comparative)

Further examples of the curing of ethylenically unsaturated monomer (25 g of pentaerythritol tetraacrylate in 225g acetonitrile) or epoxy monomer (cyclohexene oxide) are provided [illegible] curable composition consisted of 0.01g of the organometallic compound or 0.02g of diphenyliodonium hexafluorophosphate or these same amounts of both compounds added to either monomer. The light sources used were for UV exposure, about 360 nm, two 15 watt G.E. blacklite bulbs and for the visible, a Kodak Carousel Projector or the projector with a 440 nm filter. The initiation of polymerization was detected by solution gelation for the acrylate and for the epoxy the precipitation of the polymer from a 2% ammonia-methanol solution. Free radical systems were purged with N_2 for 2 minutes before and continuously during irradiation while the cationic samples were left open to the air without purging. Sample size was 2 to 3 ml in a 13 x 100 mm pyrex test tube. The results of these tests are shown in Table VIII.

TABLE VIII

Photoinitiated Cure Times of Epoxy and Acrylate Compositions[a]		
Curing Agent	Epoxy	Acrylat[illegible]
$[CpFe(CO)_2]_2$	[illegible] 90[e]	<5[illegible]
$[CpFe(CO)_2]_2$ iodonium[c]	90[d] >180[e]	<5[illegible] [illegible]
$Mn_2(CO)_{10}$	[illegible] >180[e]	[illegible]
$Mn_2(CO)_{10}$ iodonium[c]	>180[e]	[illegible]

a Cure times given in se[illegible]
b Unfiltered projector as [illegible]
c The diphenyliodonium salt showed n[illegible] itself under these same conditions
d 440 nm filter used with the projector
e Blacklite used as the light source ab[illegible]

EXAMPLE 14 (Comparative)

Examples of the photocuring of ethylenically unsaturated m[illegible] metal bond containing organometallic compounds and iodonium sa[illegible]

Samples were prepared as 1.0 g methyl acrylate contai[illegible] complex and 0.015 g $Ph_2I^+PF_6^-$. Up to 0.05 g butyrolactone [illegible] the photocatalyst systems. Samples were bubbled with N_2 a[illegible] projector with a 380 nm cutoff filter, and the time required [illegible] Alternatively, compositions could be cured thermally.

TABLE IX

Curing of Ethylenically-Unsaturated M[illegible]		
Compound and $Ph_2I^+PF_6^-$	Conditions	[illegible]
$[CpFe(CO)_2]_2$	irrad	30 sec. slow [illegible]
$Mn_2(CO)_{10}$	irrad	30 sec. no da[illegible]
$[CpMo(CO)_3]_2$	irrad	45 sec. no da[illegible]
$[Re(CO)_5]_2$	irrad	8 min. no dark
$Co_4(CO)_{12}$	irrad	Minutes slow
$Co_2(CO)_8$	Dark	Cures during

EXAMPLE 15 (Comparative)

This example describes the curing of ethylenically unsaturat[illegible] bonded organometallic compounds. Each sample was prepared [illegible]

TABLE VIII

Photoinitiated Cure Times of Epoxy and Acrylate Compositions[a]		
Curing Agent	Epoxy	Acrylate
$[CpFe(CO)_2]_2$	>180[e] 90[b]	>300[e] <5[b]
$[CpFe(CO)_2]_2$ iodonium[c]	90[d] >180[b]	<5[d] >300[b]
$Mn_2(CO)_{10}$	>180[e] >180[b]	>300[e] <10[b]
$Mn_2(CO)_{10}$ iodonium[c]	>180[e]	<10[e]

a Cure times given in seconds.
b Unfiltered projector as light source
c The diphenyliodonium salt showed no indication of polymerization by itself under these same conditions
d 440 nm filter used with the projector
e Blacklite used as the light source, about 360 nm.

EXAMPLE 14 (Comparative)

Examples of the photocuring of ethylenically unsaturated monomers using transition metal-transition metal bond containing organometallic compounds and iodonium salts are given here.

Samples were prepared as 1.0 g methyl acrylate containing 0.01 g metal-metal bond containing complex and 0.015 g $Ph_2I^+ PF_6^-$. Up to 0.05 g butyrolactone or methylene chloride were used to dissolve the photocatalyst systems. Samples were bubbled with N_2 and irradiated using a Kodak Carousel slide projector, with a 360 nm cutoff filter, and the time required to cure the sample recorded in Table IX. Alternatively, compositions could be cured thermally.

TABLE IX

Curing of Ethylenically-Unsaturated Monomers		
Compound and $Ph_2I^+ PF_6^-$	Conditions	Cure Time
$[CpFe(CO)_2]_2$	irrad.	30 sec, slow dark reaction
$Mn_2(CO)_{10}$	irrad.	30 sec, no dark reaction
$[CpMo(CO)_3]_2$	irrad.	45 sec, no dark reaction
$[Re(CO)_5]_2$	irrad.	8 min, no dark reaction
$Co_4(CO)_{12}$	irrad.	Minutes, slow dark reaction
$Co_2(CO)_8$	Dark	Cures during deoxygenation

EXAMPLE 15 (Comparative)

This example describes the curing of ethylenically unsaturated monomers with transition metal-carbon bonded organometallic compounds. Each sample was prepared by dissolving 10 mg catalyst and 20 mg

diphenyliodonium hexafluorophosphate (if used) in 0.2 g gamma-butyrolactone. 2.0 g methyl acrylate (distilled to remove inhibitors) was added in the dark and nitrogen was bubbled through the sample for 2 min to remove oxygen. Samples were then irradiated in front of a Kodak Carousel Projector containing a 360 nm cutoff filter. If no curing occurred in 15 min, the sample was then irradiated for 15 min under a Hanovia Quartz Utility lamp. In Table X, "cure time" refers to the time required for a sample to solidify. Alternatively, compositions could be cured thermally.

TABLE X

Curing of Ethylenically Unsaturated Monomer	
Curing Agent	Cure time, min
$CpPtMe_3$	15 (Hanovia)
$CpPtMe_3$ + iodonium	6 (Kodak)
$CpW(CO)_3Me$	no cure
$CpW(CO)_3Me$ + iodonium	3.5
$[CpFe(CO)_2]_2$ + iodonium[a]	0.5 (dark cure)

a included for purposes of comparison

EXAMPLE 16 (Comparative)

This example describes the use of $[CpW(CO)_3]_2$ to cure polyurethane precursors, epoxies or ethylenically unsaturated monomers. Each sample contained 0.01 g $[CpW(CO)_3]_2$ and 0.02 g diphenyliodonium hexafluorophosphate (if used) in 0.25 g gamma-butyrolactone, to which was added 2.0 g of precursor or monomer in a vial. Irradiation was then performed with a Kodak Carousel Projector (9 inches away), modified with a 360 nm filter. With a urethane precursor stock solution (prepared as in Example 4), curing to produce a clear solution; occurred in 2 hour irradiation time in the presence or absence of onium salt, partial curing. Upon standing in room light for 24 hours, an increase in viscosity occurred.

When cyclohexeneoxide was used, and the curing agent consisted of $[CpW(CO)_3]_2$ and onium salt, vigorous, exothermic curing occurred within 3 min of irradiation.

When methyl acrylate was used as monomer, no curing occurred in the absence of onium salt. With onium salt present, the sample became viscous within 4 min and solid within 8 min of irradiation time.

Alternatively, these compositions can be cured thermally.

EXAMPLE 17 (Comparative)

To demonstrate the utility of the curing agent for curing of polyurethane precursors, epoxies and vinyl monomers for the case where the organometallic compound contains a single bond between a transition metal and a Group IVA element, the following samples were prepared. In a vial, 0.01 g of organometallic compound, 0.02 g of diphenyliodonium hexafluorophosphate (if used, as indicated below), and 0.25 g of gamma-butyrolactone were gently agitated until dissolution of the organometallic compound was complete. 2.0 g of polyurethane precursors or monomer was added in reduced light, the vial was capped, and the sample irradiated in front of a Kodak Carousel projector fitted with a 360 nm cutoff filter at a distance of nine inches, and at room temperature (about 25 °C). Particular details and any experimental variations are indicated in Table XI.

TABLE XI

Cure Times: Ph toinitiated Curing f Polyurethane P
Epoxies and Vinyl Monomers ith Transition Met
Group IVA Compounds

Catalyst System	PolyUrethane[a]	Epoxy[b]
$[CpFe(CO)_2]_2$[d]	120 min (VV)[e]	f
$[CpFe(CO)_2]_2$/iodonium[d]	60 min (VV)	30 sec
$CpFe(CO)_2(CH_2Ph)$	40 min (V)	f
$CpFe(CO)_2(CH_2Ph)$/iodonium	40 min (V)	12 min
$CpFe(CO)_2(COPh)$	120 min (V)[e]	f
$CpFe(CO)_2(COPh)$/iodonium	120 min (V)[e]	[illegible] min
$CpFe(CO)_2(SiPh_3)$	45 min (V)[h]	f
$CpFe(CO)_2(SiPh_3)$/iodonium	45 min (V)[h]	5 min
$CpFe(CO)_2(GePh_3)$	36 min (V)[h]	f
$CpFe(CO)_2(GePh_3)$/iodonium	36 min (V)[h]	2.75 mi
$CpFe(CO)_2(SnPh_3)$	36 min (S)[h]	f
$CpFe(CO)_2(SnPh_3)$/iodonium	36 min (V)[h]	2 min
$CpFe(CO)_2(PbPh_3)$	45 min (S)[h]	f
$CpFe(CO)_2(PbPh_3)$/iodonium	33 min (VV)[h]	no cur

TABLE XI

Cure Times: Photoinitiated Curing of Polyurethane Precursors Epoxies and Vinyl Monomers with Transition Metal-Group IVA Compounds

Catalyst System	PolyUrethane[a]	Epoxy[b]	Vinyl[c]
$[CpFe(CO)_2]_2$ [d]	120 min (VV)[e]	f	no cure
$[CpFe(CO)_2]_2$/iodonium[d]	60 min (VV)	30 sec	1.8 min
$CpFe(CO)_2(CH_2Ph)$	40 min (V)	f	no cure
$CpFe(CO)_2(CH_2Ph)$/iodonium	40 min (V)	12 min	23 min
$CpFe(CO)_2(COPh)$	120 min (V)[e]	f	no cure
$CpFe(CO)_2(COPh)$/iodonium	120 min (V)[e]	5 min	48 hr [g]
$CpFe(CO)_2(SiPh_3)$	45 min (V)[h]	f	no cure
$CpFe(CO)_2(SiPh_3)$/iodonium	45 min (V)[h]	5 min	48 hr [g]
$CpFe(CO)_2(GePh_3)$	36 min (V)[h]	f	no cure
$CpFe(CO)_2(GEPh_3)$/iodonium	36 min (V)[h]	2.75 min	no cure
$CpFe(CO)_2(SnPh_3)$	36 min (S)[h]	f	no cure
$CpFe(CO)_2(SnPh_3)$/iodonium	36 min (V)[h]	2 min	no cure
$CpFe(CO)_2(PbPh_3)$	45 min (S)[h]	f	no cure
$CpFe(CO)_2(PbPh_3)$/iodonium	33 min (VV)[h]	no cure	no cure

a. Polyurethane precursors are from a stock solution consisting of 23.1 g of Desmodur™ W and 32.6 g of Carbowax 400. Cure times are followed by an indication in parentheses of extent of cure, where V = viscous, VV = very viscous, S = solid.

b. Monomer is cyclohexene oxide, purified by distillation. Cure time is defined as the time necessary to observe formation of precipitate when one drop of sample is placed in 2 ml of methanol.

c. Monomer is methyl acrylate, purified prior to use by distillation under reduced pressure. After monomer addition but before irradiation, samples were deoxygenated by bubbling a stream of nitrogen gas through the solution for 2 min, with care being taken to prevent any light from reaching the sample during deoxygenation. Cure is defined by an increase in solution viscosity or a sudden exotherm indicating rapid polymerization (also accompanied by a sudden increase in viscosity).

d. Included for purposes of comparison to data in other Tables.

e. 60 min irradiation with Carousel Projector, followed by 60 minutes of irradiation in room (fluorescent) light.

f. This particular combination was not tested.

g. 30 minutes irradiation with Kodak projector, following by 30 minutes irradiation unoer a Hanovia Quartz Utility Lamp (6 inches from bulb), followed by sample storage/irradiation in room (fluorescent) light.

h. Irradiation with Hanovia Quartz Utility Lamp (15 cm from bulb) in place of the Kodak Projector.

EXAMPLE 18

This example illustrates the dual curing of polyurethane precursors and ethylenically-unsaturated monomers using the curing agent $[CpFe(CO)_2]_2$ Ph_2I^+ PF_6^-.

Samples 1.25 g in size, were prepared from stock solutions of 2.08 parts Desmodur™ W (4,4'-methylenebis(cyclohexylisocyanate)), 2.92 parts polyethyleneglycol (MW = 400), 5.0 parts methyl acrylate (freshly distilled), and 0.05 parts $[CpFe(CO)_2]_2$. To half of the stock solution was added 0.082 parts Ph_2I^+

PF_6^-. Mole ratios for iodonium salt:iron dimer = 2:1; NCO:OH = 1.0; [illegible] iodonium salt = 1.2%. Samples were irradiated simultaneously using 366 nm [illegible] 10 min, then analyzed by 400 MHz ^1H nuclear magnetic resonance spectroscopy [illegible] are listed in Table XII. Curing agents comprising other combinations of [illegible] onium salts can be used in place of $[CpFe(CO)_2]_2$ and Ph_2IPF_6, respectively.

TABLE XII

Dual Curing of Polyurethane Precursors and Ethylenically Unsaturated Monomers			
Onium Salt	Conditions	Conversion to p[illegible]	
		Acrylate	Ure[illegible]
Ph_2I^+	Dark	---	
Ph_2I^+	Irradiation	[illegible]	[illegible]
Ph_2I^+	Irradiation, deoxygenated	[illegible]	[illegible]
None	Dark	[illegible]	[illegible]
None	Irradiation	24%	
None	Irradiation, deoxygenated	trace	

EXAMPLE 19

This example demonstrates simultaneous curing of ethylenically uns[illegible] Gelation times will not show that both monomers have reacted at the [illegible] nuclear magnetic reso[illegible] spectroscopy to differentiate the two polym[illegible] The experiment was carried out in the following manner: A 1:1 w/w mi[illegible] oxide was prepared. To a 10g sample of this mixture was added 0.[illegible] diphenyliodonium hexafluorophosphate (0.024g) with the iron dimer 0 [illegible] specified amounts of both compounds. In a small vial was placed 2 m[illegible] 1 min before and continually during irradiation. The light source wa[illegible] irradiation time was 2 minutes. Immediately after completion of the [illegible] taken. The amount of polymerization was determined by the ratio of [illegible] that of polymer plus monomer. The results of the study are shown in Ta[illegible]

TABLE XIII

Percent Conversion to Poly[illegible] NMR Study[a]		
Curing Agent	Epoxy	Acrylate
$[CpFe(CO)_2]_2$	0[b]	18
$[CpFe(CO)_2]_2$ iodonium	36	80
iodonium	<5	<10
$Mn_2(CO)_{10}$	<0.5	<0.5
$Mn_2(CO)_{10}$ iodonium	37	4[illegible]

a NMR's taken on a 400 MHz instrument
b None detected in the NMR

As can be seen from the NMR results, the system efficiently initiat[illegible] polymerization simultaneously. Curing agents comprising other combinatio[illegible] and onium salts can be used in place of $[CpFe(CO)_2]_2$ and $Mn_2(CO)_{10}$, and

PF_6^-. Mole ratios for iodonium salt:iron dimer = 2:1, NCO:OH = 1.0, weight % iron dimer = 0.5%, iodonium salt = 1.2%. Samples were irradiated simultaneously using 366 nm BlakRay bulbs (15 watts) for 10 min, then analyzed by 400 MHz ^1H nuclear magnetic resonance spectroscopy. Conversions to polymer are listed in Table XII. Curing agents comprising other combinations of organometallic compounds and onium salts can be used in place of $[CpFe(CO)_2]_2$ and Ph_2IPF_6, respectively.

TABLE XII

Dual Curing of Polyurethane Precursors and Ethylenically Unsaturated Monomers			
Onium Salt	Conditions	Conversion to polymer	
		Acrylate	Urethane
Ph_2I^+	Dark	—	4%
Ph_2I^+	Irradiation	79%	56%
Ph_2I^+	Irradiation, deoxygenated	78%	8%
None	Dark	0%	11%
None	Irradiation	24%	75%
None	Irradiation, deoxygenated	trace	10%

EXAMPLE 19

This example demonstrates simultaneous curing of ethylenically unsaturated monomers and epoxies. Gelation times will not show that both monomers have reacted at the same time. It is possible to use nuclear magnetic reso[illegible]e spectroscopy to differentiate the two polymers in the presence of each other. The experiment was carried out in the following manner: A 1/1, w/w, mixture of methyl acrylate/cyclohexene oxide was prepared. To a 10g sample of this mixture was added 0.01g of $[CpFe(CO)_2]_2$ or $Mn_2(CO)_{10}$, diphenyliodonium hexafluorophosphate (0.024g with the iron dimer, 0.03 g with the manganese dimer) or specified amounts of both compounds. In a small vial was placed 2 ml of the sample and it was purged for 1 min before and continually during irradiation. The light source was two 15 watt G.E. blacklite bulbs. Irradiation time was 2 minutes. Immediately after completion of the photolysis, the NMR in $CDCl_3$ was taken. The amount of polymerization was determined by the ratio of the peak intensity of the polymer to that of polymer plus monomer. The results of the study are shown in Table XIII.

TABLE XIII

Percent Conversion to Polymer from NMR Study[a]		
Curing Agent	Epoxy	Acrylate
$[CpFe(CO)_2]_2$	0[b]	18
$[CpFe(CO)_2]_2$/iodonium	36	80
iodonium	<5	<10
$Mn_2(CO)_{10}$	<0.5	<0.5
$Mn_2(CO)_{10}$/iodonium	37	47

a NMR's taken on a 400 MHz instrument.
b None detected in the NMR.

As can be seen from the NMR results, this system efficiently initiated both epoxy and free radical polymerization simultaneously. Curing agents comprising other combinations of organometallic compounds and onium salts can be used in place of $[CpFe(CO)_2]_2$ and $Mn_2(CO)_{10}$, and Ph_2IPF_6, respectively.

EXAMPLE 20

This example demonstrates the simultaneous curing of ethylenically unsaturated and epoxy monomers in a crosslinkable system. The curable composition consists of methyl acrylate, cyclohexene oxide and glycidyl acrylate. If only epoxy or acrylate cure are initiated, then this system will produce a soluble polymer. Only if both epoxy and acrylate cure are initiated will a crosslinked insoluble polymer be produced.

All monomers were distilled before use, methyl acrylate and glycidyl acrylate from hydroquinone. Sample preparations were carried out under subdued lights. The polymerizable mixture consisted of 0.2 g gamma-butyrolactone, 1.0 g glycidyl acrylate, 5.0 g methyl acrylate and 5.0 g cyclohexene oxide. Depending on the test, added to this were 0.05 g of the desired organometallic compound and/or 0.1 g diphenyliodonium hexafluorophosphate. A 3 g portion of this composition was placed in a glass vial and irradiated between two 15 watt G.E. daylight fluorescent bulbs using an Ultraviolet Products lamp holder (lamp separation distance 4 cm). The sample was purged with nitrogen for one minute preceeding and continuously during photolysis. The irradiation time required to produce a polymer insoluble in chloroform was recorded, and is noted in Table XIV. Alternatively, these compositions can be cured thermally.

TABLE XIV

Simultaneous Photoinitiation of Free Radical and Epoxy Cure in a Crosslinkable System

Compound	Cure Time[a]	
	No Onium Salt Added	Onium Salt Added
$[CpFe(CO)_2]_2$	>15	1
$CpFe(CO)_2SnPh_3$	>15	10
$CpFe(CO)_2GePh_3$	>15	15
$[CpFe(CO)_2]_2SnPh_2$	>15	10
$Mn_2(CO)_{10}$	>15	1.5
$(CO)_5MnSnPh_3$	>15	10
$[(CO)_5Mn]_2SnPh_2$	>10	4
$Re_2(CO)_{10}$	>10	5
$[CpMo(CO)_3]_2$[b]	>15	1.5
$CpMo(CO)_3SnPh_3$	>15	10

a time in minutes to produce insoluble crosslinked system. Diphenyliodonium hexafluorophosphate alone under these conditions does not produce a crosslinked system after 15 minutes.

b Only 0.01g of this compound used

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth herein.

Claims

1. An energy polymerizable composition comprising

a) at least one ethylenically-unsaturated monomer

(b) one of

(1) polyurethane precursors,

(2) at least one epoxy monomer,

c) a curing agent comprising

(1) an organometallic compound, and

(2) an onium salt, and

d) optionally, a solvent

2. The composition according to claim 1 wherein said organometallic compound has the fo

$L^1L^2L^3M$

wherein

L^1 represents none, or 1 to 12 ligands contributing pi-electrons that can be the same or … selected from substituted and unsubstituted acyclic and cyclic unsaturated compounds a… substituted and unsubstituted carbocyclic aromatic and heterocyclic aromatic compounds, ea… contributing 2 to 24 pi-electrons to the valence shell of M;

L^2 represents none, or 1 to 24 ligands that can be the same or different, contributing an … sigma-electrons selected from mono-, di-, and tri-dentate ligands, each donating 2, 4 or 6 … to the valence shell of M;

L^3 represents none, or 1 to 12 ligands that can be the same or different, each contribut… one sigma-electron each to the valence shell of each M;

Ligands L^1, L^2, and L^3 can be bridging or non-bridging ligands,

M represents 1 to 4 of the same or different metal atoms selected from the elements … IVB, VB, VIB, VIIB, and VIIIB,

with the proviso that said organometallic compound contains at least one … tal-meta… with the proviso that said organometallic compound and M are chosen so as to achieve … config… L^3; and with the proviso that L^1, L^2, L^3, and M are chosen so as to achieve … config…

3. The composition according to claims 1 and 2 wherein said onium salt has the form

AX II

wherein A is an iodonium, sulfonium, or diazonium cation, and

X is an organic sulfonate counterion, or a halogenated metal or metalloid counterion.

4. The composition according to claims 1 to 4 wherein said ethylenically-unsa… selected from the group consisting of acrylates, acrylamides and vinyl compounds.

5. The composition according to claims 1 to 4 wherein said polyurethane precurs… of polyisocyanates and compounds bearing at least two isocyanate-reactive hydroger… of isocyanate groups to isocyanate-reactive hydrogen atoms is in the range 1:2 to 2:1

6. A process comprising the steps of

a) providing a polymerizable mixture according to claims 1 to 5, and

b) allowing said mixture to polymerize or adding energy to said mixture to effe…

7. A layered structure comprising a substrate having coated on one surface t… composition according to claims 1 to 5.

8. The layered structure according to claim 7 which is an imageable structure.

9. A shaped article comprising the composition according to claims 1 to 5.

10. The composition according to claims 1 to 5 and 7 to 9 which has been …

d) optionally a solvent

2 The composition according to claim 1 wherein said organometallic compound has the formula.

$L^1L^2L^3M$

wherein

L^1 represents none, or 1 to 12 ligands contributing pi-electrons that can be the same or different ligand selected from substituted and unsubstituted acyclic and cyclic unsaturated compounds and groups and substituted and unsubstituted carbocyclic aromatic and heterocyclic aromatic compounds, each capable of contributing 2 to 24 pi-electrons to the valence shell of M.

L^2 represents none, or 1 to 24 ligands that can be the same or different contributing an even number of sigma-electrons selected from mono-, di-, and tri-dentate ligands, each donating 2, 4, or 6 sigma-electrons to the valence shell of M.

L^3 represents none, or 1 to 12 ligands that can be the same or different, each contributing no more than one sigma-electron each to the valence shell of each M;

Ligands L^1, L^2, and L^3 can be bridging or non-bridging ligands;

M represents 1 to 4 of the same or different metal atoms selected from the elements of Periodic Groups IVB, VB, VIB, VIIB, and VIIIB,

with the proviso that said organometallic compound contains at least one of a metal-metal sigma bond and L^1, and with the proviso that L^1, L^2, L^3, and M are chosen so as to achieve a stable configuration.

3 The composition according to claims 1 and 2 wherein said onium salt has the formula II

AX II

wherein A is an iodonium, sulfonium, or diazonium cation, and

X is an organic sulfonate counterion, or a halogenated metal or metalloid counterion

4 The composition according to claims 1 to 4 wherein said ethylenically-unsaturated monomer is selected from the group consisting of acrylates, acrylamides and vinyl compounds.

5 The composition according to claims 1 to 4 wherein said polyurethane precursors comprise a mixture of polyisocyanates and compounds bearing at least two isocyanate-reactive hydrogen atoms where the ratio of isocyanate groups to isocyanate-reactive hydrogen atoms is in the range 1 2 to 2.1

6 A process comprising the steps of

a) providing a polymerizable mixture according to claims 1 to 5 and

b) allowing said mixture to polymerize or adding energy to said mixture to effect polymerization

7 A layered structure comprising a substrate having coated on one surface thereof the polymerizable composition according to claims 1 to 5.

8 The layered structure according to claim 7 which is an imageable structure

9 A shaped article comprising the composition according to claims 1 to 5

10 The composition according to claims 1 to 5 and 7 to 9 which has been cured

ded to prepare the coating solution The solutions were coated onto ... chloride subbed polyester (3M Company) using a #22 wire wound ... in air, to a 275 watt G E sunlamp at a distance of 10cm The time to "set" ... that is the time needed to cure the coating so that when it is touched with ... or picks up no cotton threads This test establishes the time required ... conditions of this test, the diphenyliodonium hexafluorophosphate alone ... cure

TABLE V

Photoinitiation of Epoxy Cure		
Compound	Cure Time*	
	No Onium Salt Added	Onium Salt Added
$[CpFe(CO)_2]_2$	>10	1
$CpFe(CO)_2SnPh_3$	>10	5
$CpFe(CO)_2GePh_3$	>10	5
$[CpFe(CO)_2]_2SnPh_2$	>10	3
$Mn_2(CO)_{10}$	>10	1
$(CO)_5MnSnPh_3$	>10	4
$[(CO)_5Mn]_2SnPh_2$	>10	3
$Re_2(CO)_{10}$	1	1
$CpMo(CO)_3SnPh_3$	8	4

* time in minutes to cure

EXAMPLE 11 (Comparative)

To further demonstrate the activity of the curing agent a se... another epoxy and/or acrylate composition The organometallic ... was photolyzed in presence of an epoxy or acrylate The spe... acrylate was distilled from hydroquinone and stored cold until read... obtained from Aldrich The organometallic compounds were ... Diphenyliodonium hexafluorophosphate was recrystallized from ... done as 100% solids except as noted

In a small vial was placed 0 02 g of the organometallic com... salt along with 2 g of the desired monomer For the acrylate tests ... sec before and continuously during the photolysis The epoxy test... open to the air The light source was one 15 watt day... times represent the time required to reach the same ... Alternatively the acrylate compositions can be cured ther...